PB87-110516

Control of Sulfur Emissions from Oil Shale Retorting Using Spent Shale Absorption

J and A Associates, Inc., Golden, CO

Prepared for

Environmental Protection Agency
Research Triangle Park, NC

Oct 86

U.S. Department of Commerce
National Technical Information Service
NTIS

PB87-110516

EPA/600/7-86/032
October 1986

CONTROL OF SULFUR EMISSIONS FROM OIL SHALE RETORTING USING SPENT SHALE ABSORPTION

by

K. D. VanZanten and F. C. Haas
J&A Associates
Golden, Colorado 80401

Contract No. 68-03-1969

Project Officer

Edward R. Bates
Air and Energy Engineering Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, N.C. 27711

Air and Energy Engineering Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL
INFORMATION SERVICE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600/7-86/032	2.	3. RECIPIENT'S ACCESSION NO. PB87 110516/AS
4. TITLE AND SUBTITLE Control of Sulfur Emissions from Oil Shale Retorting Using Spent Shale Absorption		5. REPORT DATE October 1986
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) K.D. VanZanten and F.C. Haas		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS J and A Associates 18200 W. Highway 72 Golden, Colorado 80401		10. PROGRAM ELEMENT NO.
		11. CONTRACT/GRANT NO. 68-03-1969
12. SPONSORING AGENCY NAME AND ADDRESS **EPA, Office of Research and Development** Air and Energy Engineering Research Laboratory Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Final; 10/85-2/86
		14. SPONSORING AGENCY CODE EPA/600/13

15. SUPPLEMENTARY NOTES AEERL project officer is Edward R. Bates, Mail Drop 62B, 919/541-2853.

16. ABSTRACT The report describes an investigation of the environmental advantages/disadvantages of absorbing SO2 onto combusted retorted oil shale. The objective of this program was to obtain more information in support of Prevention of Significant Deterioration (PSD) permitting decisions on sulfur control and to determine if the emission of other pollutants such as nitrogen oxides (NOx) and trace elements is significantly increased by the combustion process. The program consists of two phases: Phase I developed an engineering assessment and costs for application of this sulfur absorption process to selected leading retorting processes, and Phase II was experimental work in an integrated oil shale pilot plant to define operability, proof of principle, and trace element emissions. Based on the pilot plant data obtained in this study, fluid bed operating conditions are recommended to optimize SO2 and NOx control. In general, conditions that favor low SO2 emissions also favor low CO and trace hydrocarbon emissions, but do not favor low NOx emissions. The general ranges of operating conditions which produced reasonable results from both operating and emissions viewpoints are given in the report. Results of the trace element tests indicated some relative trends with regard to emissions but, because of the brevity of the sampling, no hard conclusions can be reached for extrapolation to the long term.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Pollution Control	13B
Oil Shale	Stationary Sources	08G
Combustion	Retorting	21B
Sulfur	Spent Shale	07B
Emission		14G
Absorption		

18. DISTRIBUTION STATEMENT **Release to Public**	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 133
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (9-73)

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ABSTRACT

Control of sulfur emissions constitutes a major portion of the environmental control cost for oil shale facilities. These substantial sulfur control costs have encouraged developers to seek less costly but equally or more effective methods for limiting sulfur emissions. Recently a strong industry trend has been to look toward the potential for combusting carbonaceous retorted shale to recover its energy value (a plus in terms of economics and resource conservation), while exploring the possibility of absorbing the sulfur gases produced during retorting onto the calcined carbonate material present after combustion of retorted western oil shale.

This study investigated the environmental advantages/disadvantages of absorbing SO_2 onto combusted retorted oil shale. The objective of this program was to obtain more information in support of PSD permitting decisions on sulfur control and to investigate whether emission of other pollutants such as nitrogen oxide (NO_x) and trace elements might be significantly increased by the combustion process. The program was done in two phases. Phase I developed an engineering assessment and costs for application of this sulfur absorption process to selected leading retorting processes. In Phase II, experimental work in an integrated oil shale pilot plant defined operability and proof of principle and defined trace element emissions.

Based on the pilot plant data obtained in this study, fluid bed operating conditions are recommended to optimize SO_2 and NO_x control. In general, conditions that favor low SO_2 emissions also favor low CO and trace hydrocarbon emissions but do not favor low NO_x emissions. The general ranges of operating conditions which produced reasonable results both from an operating and emissions viewpoints are given in the report. Results of the trace element tests indicated some relative trends with regard to emissions but because of the short duration of the sampling, no hard conclusions can be reached which would allow extrapolation of results to long term steady-state operations.

TABLE OF CONTENTS

Page

Abstract. iii
Figures. vii
Tables. viii
Tables in Appendix A. x
Abbreviations and Symbols. xi
English/Metric Conversions. xii

I. INTRODUCTION

A. Background. 1
B. Conventional Sulfur Control Technologies. . . . 2
C. The Absorption on Spent Shale Concept. 3
D. ASSP Process Description. 4
E. Phase I - Engineering Evaluation/Conceptual Process Design. 4
F. Phase II - Pilot Plant Program. 6

II. SUMMARY AND CONCLUSIONS

A. Phase I Conceptual Design and Economics. 8
B. Phase II Pilot Plant Testing. 9

III. CONCEPTUAL DESIGN AND ECONOMICS

A. Design Basis. .13
B. Costs. 17

IV. PILOT PLANT TESTING

A. Description of the Pilot Plant. 24
B. Plant Instrumentation. 26
C. Experimental Procedure. 26
D. Discussion of Results. 31
E. Process Variable Correlations. 34
F. Trace Element Sampling and Analyses. 48

V. RECOMMENDATIONS ON DESIGN AND OPERATION OF A FLUID BED COMBUSTOR WHICH OPTIMIZES SO_2 and NO_x CONTROL. . 57

VI. QUALITY ASSURANCE/QUALITY CONTROL

A. QA Objectives and Performance. 59
B. Sampling Methodology and Results. 61
C. Analytical Methodology and Results. 64
D. Trace Element Methodology and Results. 69

TABLE OF CONTENTS (Continued)

Page

VII. REFERENCES. 71

APPENDIX A - Data from Fluidized Bed Tests. 73

APPENDIX B - Leaching and Hydraulic Properties of Three Baghouse Ash Samples. 103

LIST OF FIGURES

Number Page

1. ASSP Process Flow Diagram 5
2. Effect of Flue Gas Oxygen on SO_2 and NOx Emissions 11
3. Effect of Flue Gas Oxygen on CO and Trace Hydrocarbon Emissions 11
4. Process Flow Diagram for ASSP Evaluation - Direct Heated (Modified In-Situ with Unishale C). . 14
5. Process Flow Diagram for ASSP Evaluation - Indirect Heated (Unishale B) 15
6. Process Flow Diagram for ASSP Evaluation - Integral Part of Process (Lurgi). 16
7. Pilot Plant Process Flow Diagram 25
8. Effect of Flue Gas Oxygen on SO_2 Emissions 36
9. Effect of Flue Gas Oxygen on NO_x Emissions 37
10. Effect of Flue Gas Oxygen on CO Emissions 38
11. Effect of Flue Gas Oxygen on Trace Hydrocarbon Emissions 40
12. Effect of Flue Gas Oxygen on Baghouse Ash Organic Carbon 41
13. Effect of Solids Residence Time on SO_2 Emissions. 42
14. Effect of Solids Residence Time on NO_x Emissions. 43
15. Effect of Solids Residence Time on CO Emissions . . .44
16. Effect of Fluid Bed Temperature on SO_2 Emissions . . 45
17. Effect of Fluid Bed Organic Carbon on Organic Carbon Combustion Efficiency 46
18. Effect of Baghouse Ash Organic Carbon on Organic Carbon Combustion Efficiency 47
19. Sampling Train for Recycle Retort Gas and Flue Gas. .49
20. Comparison of Flue Gas Oxygen Analyses. 68

LIST OF TABLES

Number Page

1. Cost Comparison for ASSP 9
2. Equipment Changes for ASSP 17
3. Conceptual Design Bases 18
4. Major Parameters Used in ASSP Conceptual Designs . . 19
5. Incremental Capital Cost for ASSP Conceptual Designs 20
6. Incremental Operating Costs for ASSP Conceptual Designs 21
7. Incremental Capital and Operating Costs for ASSP Conceptual Designs 22
8. Properties of Raw Shale Used in Combustor Tests . . .27
9. Range of Operating Conditions and Process Vriables . 31
10. Range of Flue Gas Composition and Organic Carbon Combustion Efficiency 31
11. Range of Solids Composition 32
12. Mass Flow Rate Measurements 33
13. Process Variable Correlations 35
14. Trace Element Analyses from Pilot Plant Tests 7, 12 and 19C 51
15. Summary of Elemental Balances Around Combustor . . . 52
16. Percentage of Trace Elements Present in Raw Shale Found in Retort Gas and Flue Gas 53
17. Percent Distribution of Total Element Concentration in Gas Stream Found in Various Scrubbers 56
18. Comparison of Fluid Bed Combustor Operating Conditions 57
19. Comparison of Test 19C Operating Conditions with Conceptual Design 58

19a. Summary of Precision Accuracy and Completeness Objectives 60

LIST OF TABLES (Continued)

Number Page

20. Sample of Analyses and Frequency of Analysis 61

21. Summary of Duplicate Mineral Carbon Analyses 64

22. Summary of Duplicate Total Carbon, Hydrogen and Nitrogen Analyses 64

23. Summary of Duplicate Sulfur Analyses 65

24. Summary of Spike Recoveries 65

25. Summary of Spike Recoveries 69

26. Summary of Duplicate Analyses 70

LIST OF TABLES IN APPENDIX A

Number Page

A-1 Summary of Fluid Bed Combustor Tests 74

A-2 Fluid Bed Combustor Operating Conditions. 77

A-3 Properties of Retorted Solids Feed to Combustor 80

A-4 Properties of Combusted Shale (Heat Carrier) from Combustor 81

A-5 Properties of Combusted Fines (Baghouse Ash) from Combustor 82

A-6 Elemental Analysius of Selected Solids by X-ray Fluorescence 83

A-7 Analysis of Natural Gas and Retort Gas Used in Combustor Tests. 84

A-8 Combustor Flue Gas Composition and Flow Rates 87

A-9 Overall Mass Flow Balances. 90

A-10 Total Carbon Balances. 92

A-11 Mineral Carbon Balances 93

A-12 Organic Carbon Balances 94

A-13 Sulfur Balances 95

A-14 Nitrogen Accountability in Solids and Flue Gas NO_x 96

A-15 Mercury Balances Around Combustor 97

A-16 Cadmium Balances Around Combustor 98

A-17 Arsenic Balances Around Combustor 99

A-18 Lead Balances Around Combustor 100

A-19 Beryllium Balances Around Combustor 101

A-20 Fluoride Balances Around Combustor 102

LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

AA -- Atomic Absorption
ASSP -- Absorption on Spent Shale Process
DEA -- Diethanolamine
FGD -- Flue gas desulfurization
ft/sec -- Feet per second
g/hr -- Grams per hour
g/l -- Grams per liter
GPT -- Gallons per ton
HSP -- Hydrocarbon Solids Processing
kg/hr -- Kilograms per hour
lb/hr -- Pounds per hour
LTPSD -- Long tons per stream day
m^3/hr -- Cubic meters per hour
MDEA -- Methyldiethanolamine
mg/hr -- Milligrams per hour
MIS -- Modified in-situ
ml -- Milliliter
ppm -- Parts per million
ppmv -- Parts per million by volume
SCFM -- Standard cubic feet per minute
TPSD -- Tons per stream day
ug/m^3 -- Micrograms per cubic meter
v% -- Volume percent
vol% -- Volume percent
wt% -- Weight percent

SYMBOLS

As -- Arsenic
Be -- Beryllium
Ca -- Calcium
Ca/S -- Calcium to sulfur mole ratio
$CaCO^3$ -- Calcium carbonate
$CaMg(CO_3)_2$ -- Calcium magnesium carbonate (dolomite)
Cd -- Cadmium
CO -- Carbon monoxide
CO_2 -- Carbon dioxide
COS -- Carbonyl sulfide
CS_2 -- Carbon disulfide
F -- Flourine
FeS -- Iron (ferrous) sulfide
FeS_2 -- Iron (ferric) sulfide
H_2S -- Hydrogen sulfide
Hg -- Mercury
HNO_3 -- Nitric acid
Mg -- Magnesium
$MgCO_3$ -- Magnesium carbonate
N_2 -- Nitrogen
NaOH -- Sodium hydroxide
NH_3 -- Ammonia
NO_x -- Nitrogen oxides
O_2 -- Oxygen
Pb -- Lead
SO_2 -- Sulfur dioxide

ENGLISH/METRIC CONVERSIONS

TO CONVERT ENGLISH UNIT	INTO SI METRIC UNIT	MULTIPLY BY
Barrels	Cubic Meters	0.159
Cubic Feet	Cubic Meters	0.02832
Day	Seconds	86,400
Degrees Celcius	Degrees Kelvin	$^oC + 273$
Degrees Fahrenheit	Degrees Kelvin	$(^oF-32)x1.8+273$
Feet	Meters	0.3048
Gallons	Cubic Meters	0.003785
Hours	Seconds	3600
Inches	Meters	0.0254
Minutes	Seconds	60
Pounds	Kilograms	0.4536
Tons	Kilograms	907.18

I. INTRODUCTION

A. Background

Control of sulfur emissions is a key environmental concern in the retorting of oil shale. Oil shale may contain 2% or more sulfur, while a typical shale in the Green River Formation of Colorado contains about 0.7% sulfur. Although this sulfur concentration is not large compared to some high sulfur coals (4 to 8% sulfur), large-scale production of shale oil will require processing millions of tons of oil shale; thus, sulfur emissions would be very great if controls were not applied. About 16 to 30% of the sulfur in oil shale is liberated to the vapors (oil and gas) produced during retorting, and the remainder stays with the spent shale. Retort gasses generally contain hydrogen sulfide (H_2S) as the major sulfur compound and lesser amounts of other organic sulfur compounds such as sulfur dioxide (SO_2), carbonyl sulfide (COS), carbon disulfide (CS_2), and mercaptans (CH_3SH and C_2H_5SH).

To date, the federal government has not promulgated New Source Performance Standards for the oil shale industry. However, the U.S. Environmental Protection Agency does regulate SO_2 (and some other emissions) through Prevention of Significant Deterioration (PSD) permitting requirements of the Clean Air Act. This legislation requires use of Best Available Control Technology - cost considered (BACT) to minimize the addition of specified pollutants in order to preserve air quality. PSD permits are issued on a facility by facility basis after careful analysis of each application. The federal PSD requirement that generally is most difficult for developers to meet is the 24 hour Class I air quality standard limiting SO_2 to 5 g/m^3. In addition to federal requirements, states also control the emission of SO_2 from oil shale facilities. For example, the State of Colorado limits SO_2 emissions to less than 0.3 pound of SO_2 per barrel of shale oil produced.

Control of sulfur emissions has been estimated to constitute a major portion of the environmental control cost for oil shale facilities. For example, the Denver Research Institute estimated costs (in 1980 dollars) in the range of $1 to $3 per barrel of shale oil produced (1,2). These substantial sulfur control costs have encouraged developers to seek less costly but equally or more effective methods for limiting sulfur emissions. Recently, a strong industry trend has been to look toward the potential for combusting carbon on carbonaceous retorted shale to recover its energy value (a plus in terms of economics and resource conservation), while exploring the possibility of absorbing the sulfur gases produced during retorting onto the calcined carbonate material present after combustion of retorted western oil shale.

This study investigated the environmental advantages/disadvantages of absorbing SO_2 onto combusted retorted oil shale. The objective of this program was to obtain more information in support of PSD permitting decisions on sulfur control and to investigate whether emission of other pollutants such as nitrogen oxide (NO_x) and trace elements might be significantly increased by the combustion process. The program was done in two phases. Phase I developed an engineering assessment and costs for application of this sulfur absorption process to selected leading retorting processes. In Phase II, experimental work in an integrated oil shale pilot plant defined operability and proof of principle and defined trace element emissions.

B. Conventional Sulfur Control Technologies

Two approaches have generally been used to control sulfur emissions from retort gases -- removal of the sulfur compounds from the gas before it is combusted (gas sweetening) or combustion of the gas followed by removal of the SO_2 from the flue gases (flue gas desulfurization).

Gas sweetening processes such as amine absorption and Stretford generally are very effective in removing H_2S. However, organic sulfur compounds, principally COS, are not significantly removed or are only partly removed by these conventional processes. While H_2S levels are reduced to about 10 ppmv in the sweet gas, overall sulfur removal efficiencies are lower (95-98%) because the organic sulfur compounds are not completely removed.

Flue gas desulfurization (FGD) processes, which use an aqueous slurry of lime to absorb SO_2 from the flue gas, generally are not as highly effective in removing SO_2. Typical SO_2 removal efficiencies range from 90 to 95%. In addition, FGD processes must handle larger volumes of gas than gas sweetening processes.

To meet Colorado's air quality regulations of 0.3 lb. SO_2/bbl of shale oil produced, about 95-96% of the total sulfur in the gas would have to be removed. This makes use of FGD processes marginal and tends to focus more interest on gas sweetening processes. However, gas sweetening plants are generally expensive to build and operate, and the sulfur product recovered may not be saleable because of product impurities or the remoteness of the oil shale plants from traditional sulfur markets.

The practicality of conventional control technologies applied to oil shale plants depends to a great extent on the type of retorting process employed; i.e., direct heated vs. indirect heated. Direct heated retorts are those in which direct combustion with air occurs inside the retort to supply the heat of retorting. Examples of such processes are Modified In-Situ (MIS), Paraho Direct Heated, and Union A. Indirect heated retorts provide heat using heated gases or solids and no combustion occurs in the retort vessel. Examples are Union B and C, Tosco II, Lurgi, and Chevron STB.

In direct heated retorts, sulfur is liberated mostly as H_2S, but the off-gases are relatively dilute in hydrocarbons because large quantities of N_2, O_2, CO_2, and H_2O are liberated from combustion. H_2S removal from such gas streams is quite expensive using conventional gas sweetening technologies and in some cases is economically prohibitive. Non-selective processes (i.e., processes which co-sorb both H_2S and CO_2) are unattractive because of the very great cost associated with removing the large quantities of CO_2. Selective processes (selective for H_2S), such as Stretford, are more economically attractive, but there remain numerous technical concerns about Stretford-type processes with regard to solvent degradation, quality of product sulfur, spent solvent disposal, etc.

From a sulfur emissions viewpoint, indirect heated retorts are less problematic with respect to gas treatment, but there are a number of problem areas. Indirect heated retorts produce gases with relatively little CO_2 (although higher than natural or refinery gases), and don't have O_2 or N_2 as diluents. Proposed treating plants for indirect heated retorts use conventional processes such as amine sweetening or other processes typically applied to handling natural or refinery gases. Typically, regenerated H_2S streams end up in a Claus sulfur plant with tail gas treatment. Design of a Claus plant as applied to oil shale gas treating is complicated by quantities of both NH_3 and CO_2, which are higher than in natural or refinery gases. Also, virtually none of the conventional gas sweetening processes do much to remove sulfur species other than H_2S; e.g., COS, CS_2, and mercaptans. For the most part, these remain in the gas which, when burned, end up as SO_2 in the stack. All of these conventional treating plants are more expensive to build and operate than comparable systems in refineries and gas plants because of the higher levels of CO_2, and to a lesser extent, because of higher levels of NH_3 and unsaturated hydrocarbons.

C. The Absorption on Spent Shale Concept

Retorted shale contains from 4 to 10 wt% organic carbon, and research efforts have been directed to recovering this energy by combusting the shale, usually in a fluid bed or other fluidized transport device. Initially there was some concern that excessive sulfur emissions might result because the retorted shale contains approximately 0.7 wt% sulfur in the form of organic sulfur, pyrite (FeS_2), and/or pyrrhotite (FeS). However, it was soon discovered that sulfur emissions were very low when combusting carbonate-containing retorted shale. Approximately half the mineral content of Green River oil shale consists of dolomite [$CaMg(CO_3)_2$] and calcite ($CaCO_3$). These two minerals are the essential components of calcareous rocks used in controlling SO_2 in coal combustion. These carbonates in oil shale are fine-grained, with grain sizes ranging from 1 to 10 microns which is desirable since fine-grained calcareous rocks are generally better SO_2 sorbents than the coarse grained rocks.

A number of laboratory and small pilot scale experiments have been conducted to test the ability of carbonate-containing shales to control sulfur emissions. For example, McCarthy(3) conducted experiments in a four inch diameter fluidized bed burning raw shale fines and sulfur containing gases. He found that at 810-820°C, a 0.2 v% H_2S gas could be burned, emitting less than 1 ppmv sulfur as SO_2.

This ability of combusted carbonate-containing spent shale to absorb SO_2 gives rise to a novel concept for controlling sulfur emissions in oil shale plants. This concept will be referred to as ASSP which stands for Absorption on Spent Shale Process.

The ASSP concept has several potential advantages over conventional sulfur removal technologies:

- The sorbent is cheap and inherently abundant in oil shale plants.
- The process requires combustion of the spent shale which is already incorporated into several of the retorting technologies or which would be a useful add-on to recover residual carbon values.
- Since non-H_2S compounds are converted to SO_2 by combustion, ASSP could represent a more efficient removal relative to gas sweetening processes which only remove H_2S.

D. ASSP Process Description

The ASSP concept uses a fluidized transport system to combust either raw or retorted shale, thereby providing the vehicle for converting sulfur compounds to SO_2 and absorbing the SO_2 in the shale matrix. The concept envisions either a conventional dense-phase fluidized bed or a dilute-phase contactor (lift pipe). Key elements of the process are shown in Figure 1.

Solids feed is either crushed raw shale or retorted shale with a top size of 1/4-inch or a mixture of raw and retorted shale. Air is introduced at the bottom of the contactor along with process and/or waste gases to be treated. The contactor is provided with coils for removing heat. Heat removed is used either for heating process gas streams or for raising steam. Cyclones, flue gas coolers, scrubbers, and/or baghouses are provided for recovering heat and removing dust from the combuster flue gas.

NO_x emissions are controlled by staged combustion; i.e., an oxygen-lean first stage followed by an oxygen-rich second stage.

Spent gas is discharged and cooled for heat recovery and moisturized prior to disposal.

E. Phase I - Engineering Evaluation/Conceptual Process Designs

The engineering assessment of the ASSP concept completed during Phase I evaluated three types of retorting processes:

- Direct heated
- Indirect heated
- Indirect heated with combustion integrated into the process

Specific retorting technologies and sites were selected as representative of these three retort types, as follows:

Retort Type	Process	Site
Direct heated	MIS with Unishale C	Cathedral Bluffs (Tract C-b)
Indirect heated	Unishale B	Union Oil (Parachute Creek)
Integral combustor	Lurgi	Rio Blanco (Tract C-a)
Integral combustor	Unishale C*	Union Oil

* The Unishale C Process is Unishale B with the addition of a fluid bed combustor.

The conclusions of this engineering assessment are given in Section II and discussed in more detail in Section III.

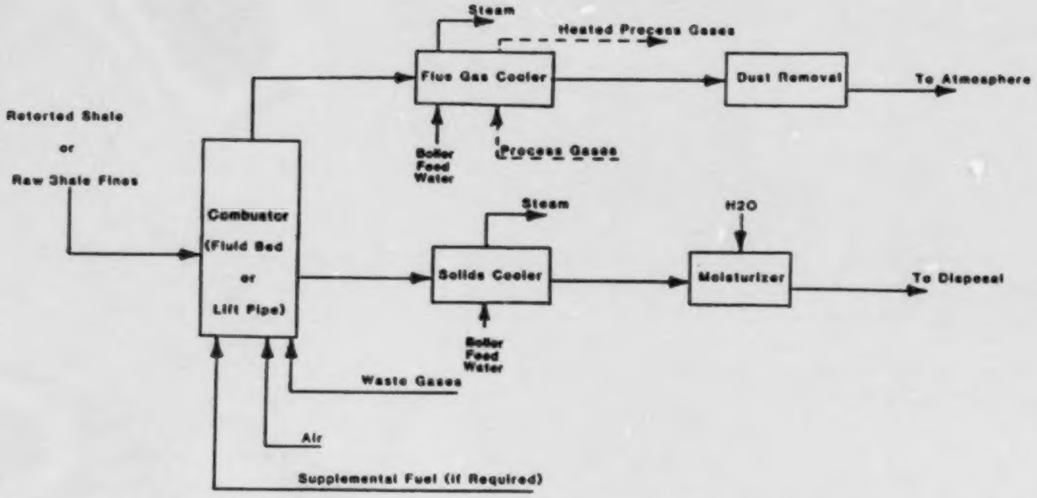
Steam
Heated Process Gases
Flue Gas Cooler
Dust Removal
To Atmosphere
Retorted Shale
or
Raw Shale Fines
Boiler
Feed
Water
Process Gases
Combustor
(Fluid Bed
or
Lift Pipe)
Steam
H2O
Solids Cooler
Moisturizer
To Disposal
Boiler
Feed
Water
Waste Gases
Air
Supplemental Fuel (if Required)

FIGURE 1
ASSP PROCESS FLOW DIAGRAM

F. Phase II - Pilot Plant Program

Phase II of the EPA contract involved pilot scale experimental testing of the ASSP concept. The test facility used in Phase II was a pilot plant used by Tosco Corporation to develop their Hydrocarbon Solids Processing (HSP) process(4). The pilot plant has a nominal capacity of six tons per day of oil shale and contains a fluidized bed combustor which is eighteen inches in diameter. A process description of the pilot plant is given in Section IV.

Key questions addressed in the Phase II test program included:

- How effective is ASSP in controlling sulfur emissions?
- Will ASSP produce large quantities of NO_x?
- What are the most favorable operating conditions to achieve maximum sulfur control while holding NO_x emissions to a minimum?
- Will retorted or raw oil shale combustion produce significant emissions of trace elements such as mercury or cadmium?

The Phase I engineering assessment evaluated application of the ASSP concept to several types of retorts which would either incorporate a lift pipe or a fluidized bed combustor as an integral part of the process. The Phase II pilot plant program studied the burning of retort gas in a fluidized bed combustor which was integrated into the retorting process, i.e., the combustor provides retort heat by burning residual carbon on spent shale and the spent shale is returned as hot solids to the retort.

The pilot plant was operated for ten days between October 14 and 25, 1985. The pilot plant was operated three shifts per day, five days a week, Monday through Friday. Each shift consisted of three operators and one shift engineer. Operator duties included operating the plant, recording all data and taking samples. See Section VI Part A for a description of the sampling procedures used for these tests.

A total of 44 "tests" were conducted during which plant operating data was recorded. Solid and gas samples were taken on 27 of these tests.

Twenty tests were selected for further evaluation by submitting the solids samples for chemical analysis. Eight of these tests were analyzed fairly completely and the other 12 were subjected to less extensive analysis. The solids and gases exiting the combustor from three tests were analyzed for six trace metals. Large (5-gallon) samples of combustor fines were also collected during three other tests for leaching studies at Colorado State University (See Appendix B). Conclusions from the pilot plant program are given in Section II and a discussion of the pilot plant results is given in Section IV.

Total carbon, mineral carbon, organic carbon, and sulfur balances were completed on the twenty tests selected for more complete evaluation. Mass rate balances were calculated on all 44 tests, i.e., pounds per hour of all solid and gas streams entering and leaving the fluid bed combustor. Trace element balances for six trace metals were also calculated for three of the tests.

Correlations of selected process variables and their effect on SO_2 and NO_x emissions and other key dependent variables were prepared and are discussed in Section IV. Recommendations on design and operation of a fluid bed combustor for SO_2 and NO_x control are given in Section V. A discussion of quality assurance/quality control procedures as applied to sampling and analysis is given in Section VI. Tables containing detailed information on test operating conditions, sample analyses, mass flow balances and trace element balances are given in Appendix A.

II. SUMMARY AND CONCLUSIONS

The results of the Phase I study indicate that the ASSP concept is technically and economically viable compared to conventional sulfur removal technologies for most oil shale retorting processes. The results of the Phase II pilot program indicate that the ASSP concept is quite effective in controlling sulfur emissions and with carefully controlled operating conditions, NO_x emissions can also be reduced by more than 85 percent. The pilot plant program also determined that some trace elements are volatilized by fluid bed temperatures in the range of 1240 to 1550°F.

A. Phase I Conceptual Design and Economics

For evaluation purposes, specific projects were chosen as representative of the three retort types:

- o Direct heated - MIS with Unishale C - Cathedral Bluffs
- o Indirect heated - Unishale B - Union Oil
- o Integral Combustor - Lurgi - Rio Blanco
  - Unishale C - Union Oil

This study assumed that MDEA amine absorption B used to remove acid gases from indirect heated retort gases and that regenerated acid gases are burned in the ASSP combustor. MIS gases were assumed to be processed on the ASSP combustor without pretreatment.

For comparison purposes, conventional sulfur removal processes were evaluated:

- o Direct heated - Case A: Unisulf + Flue Gas Desulfurization on MIS gases
  - Case B: Unisulf + Stretford on MIS gases
- o Indirect heated - Unisulf
- o Integral Combustor - DEA + Stratford on Lurgi
  - Unisulf on Unishale C

Major equipment costs were taken frm EPA Pollution Control Technical Manuals (PCTM). ASSP equipment were sized and costs factored from in-house data and PCTMs. Costs were factored to first quarter 1985.

Results of the cost study showed changes in incremental capital and operating costs for ASSP relative to conventional processing in Table 1 below:

TABLE 1. COST COMPARISON FOR ASSP

Retort Type	Direct Heated Case A, Case B		Indirect Heated	Integral Combustor	
Retorting Process	MIS/Unishale C		Unishale B	Lurgi	Unishale C
ASSP Incremental Capital Cost	-71.2	63.2	+90.2	-13.0	-32.1
$\$10^6$ Relative to Conventional Base					
ASSP Incremental Annual Operating Cost, $\$10^6$ Relative to Conventional	+10.83	+12.07	-19.21	-2.29	-1.56

These cost comparisons show that the best potential for application of ASSP are those processes which already have a spent shale combustor integrated into the retorting process (e.g., Lurgi, Unishale C, Chevron STB, and Tosco HSP). Capital and operating cost savings for Unishale C and Lurgi cases are primarily a result of deleting the Unisulf and Stretford plants.

Economics for indirect and direct heated retorts are good to marginal. Factors which will affect the economics are:

- How effective by combustor heat can be utilized (simple steam raising is the least desirable)
- The value of steam
- The use of fast or circulating fluid beds to reduce investment in combustor equipment

B. Phase II Pilot Plant Testing

Pilot plant tests were performed in a bubbling fluid bed combustor of the type which is integrated into the retort process. A total of 44 individual tests were performed. Variables evaluated were combustor temperature, solids residence time, gas residence time, oxygen concentration, inlet gas sulfur concentration, staged combustion, and raw shale injection. Over the entire range of conditions tested, emissions of primary pollutants were:

Component	Range
SO_2	1-38 ppmv
NO_x	80-670 ppmv
CO	0.05-1.80 vol%
Trace Hydrocarbons	51-8465 ppmv

Key findings of the tests were:

- SO_2 emissions were easily controlled to low levels at virtually all conditions tested probably as a result of the high Ca/S ratios used.
- NO_x emissions were primarily sensitive to oxygen concentration (Figure 2). Reasonably good NO_x control could be obtained with flue gas oxygen concentrations below about 3 vol%. The lowest NO_x concentrations were seen at O_2 levels approaching zero but at the expense of higher CO and trace hydrocarbon emissions.
- CO and trace hydrocarbon emissions were primarily sensitive to flue gas oxygen concentration (Figure 3). Good control of both could be obtained at O_2 levels above about 2 vol%.

Emissions of NO_x and SO_2 move in a direction opposite to CO and trace hydrocarbon emissions. Thus finding a set of operating conditions which minimize all four represents a compromise. One test was run which produced nearly optimum results. Conditions for this test were:

Bed Temperature	1227°F
Solids Residence Time	9.4 min.
Gas Residence Time	0.9 sec.
Gas Supply Velocity	44 ft/sec
Flue Gas O_2	2.6 vol%
Ca/S Mole Ratio	10.3
Raw Shale/Spent Shale Ratio	1:36

At these conditions the following results were obtained:

SO_2	11 ppmv
NO_x	160 ppmv
CO	0.27 vol%
Trace Hydrocarbon	388 ppmv
Combustion Efficiency	89%

During selected tests, both combustor flue gas and retort gas were sampled and analyzed for selected trace elements--mercury, cadmium, arsenic, lead, beryllium and fluoride. During these tests, solids streams were also analyzed for trace elements in an attempt to determine where trace elements go. One run was performed where a spike solution of mercury and cadmium was added to the combustor.

Results of the trace element tests indicated some relative trends with regard to emissions but because of the short duration of the sampling, no hard conclusions can be reached which would allow extrapolation of results to long term steady-state operations. Some of the key observations were:

- Lead, beryllium and fluoride were found to have low volatility. That is, of the amounts present in raw shale, only very small percentages were volatized to the gas streams.
- Arsenic was found in significant concentrations in the retort gas (100-400 ppmv) although the amount of arsenic represented less than 15% of that in the raw shale.

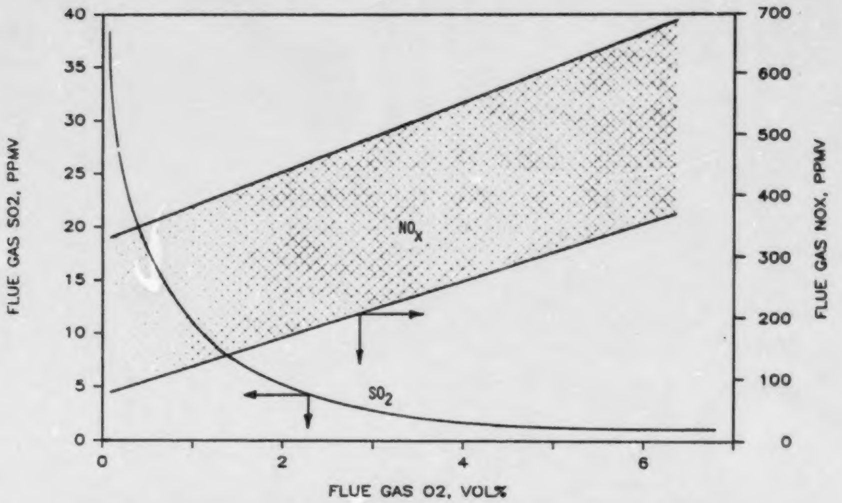

Figure 2. Effect of flue gas oxygen on SO_2 and NO_x emissions.

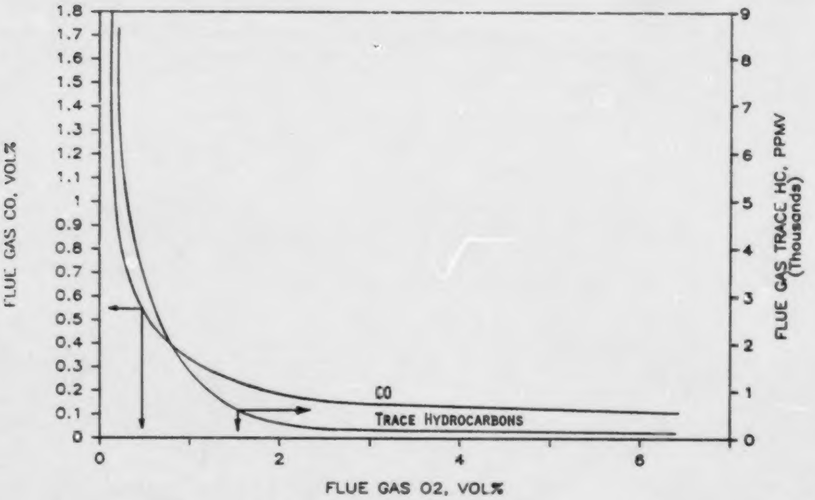

Figure 3. Effect of flue gas oxygen on CO and trace hydrocarbon emissions.

- So little mercury was present in the raw shale that mercury emissions could not be characterized with high accuracy. Mercury emissions were very low except during the spike indicating that mercury, if present in higher concentrations in the raw shale, could possibly pose emissions problems.

- Cadmium demonstrated moderate volatility at higher retort and combustor temperatures but emissions represented less than 10% of cadmium present in raw shale.

There is some evidence that mercury and cadmium introduced to the combustor during the spike test condensed within the retort equipment and revolatized over time. However, because of the limited number of samples taken, it would not be prudent to draw any hard conclusions. Longer term steady-state operations would have to be studied to determine the fate of mercury and cadmium with more certainty.

III. CONCEPTUAL DESIGN AND ECONOMICS

A. Design Basis

For study purposes, specific retorting technologies and sites were selected as representative of the direct heated, indirect heated and integrated combustor types:

Retort Type	Process	Site
Direct heated	MIS with Unishale C	Cathedral Bluffs (Tract C-b)
Indirect heated	Unishale B	Union Oil (Parachute Creek)
Integral combustor	Lurgi	Rio Blanco (Tract C-a)
Integral combustor	Unishale C*	Union Oil (Parachute Creek)

* The Unishale C process is Unishale B with the addition of a fluid bed combustor.

Simplified block flow diagrams for each study case are given in Figures 4, 5 and 6.

The study assumed that an amine process is used to remove acid gases (H_2S and CO_2) from indirect heated retort gases. The regenerator acid gases are then processed in either a fluidized bed combustor (Unishale C process) or a lift pipe combustor (Lurgi process) where spent shale and/or raw shale fines are burned to supply some of the retorting heat requirements. Modified in-situ retort gases are processed directly in a fluidized bed combustor without any pretreatment.

For each type of retort studied, a conceptual process design was developed to evaluate the potential effectiveness and cost of applying the ASSP process on a commercial scale. Conventional sulfur removal processes, which are either being planned or are currently in use, were also evaluated. The capital and operating costs of the ASSP process were then compared to these conventional sulfur removal processes.

Conventional processes evaluated were:

Retort Type	Retort Process	Conventional Treating Process
Direct heated	MIS + Unishale C	Case A: Unisulf + Flue Gas Desulfurization on MIS gases Case B: Unisulf + Stretford on MIS gases
Indirect heated	Unishale B	Unisulf*
Integral combustor	Lurgi	Diethanolamine (DEA) + Stretford
Integral combustor	Unishale C	Unisulf

* Unisulf is a Union Oil Company proprietary sulfur removal process

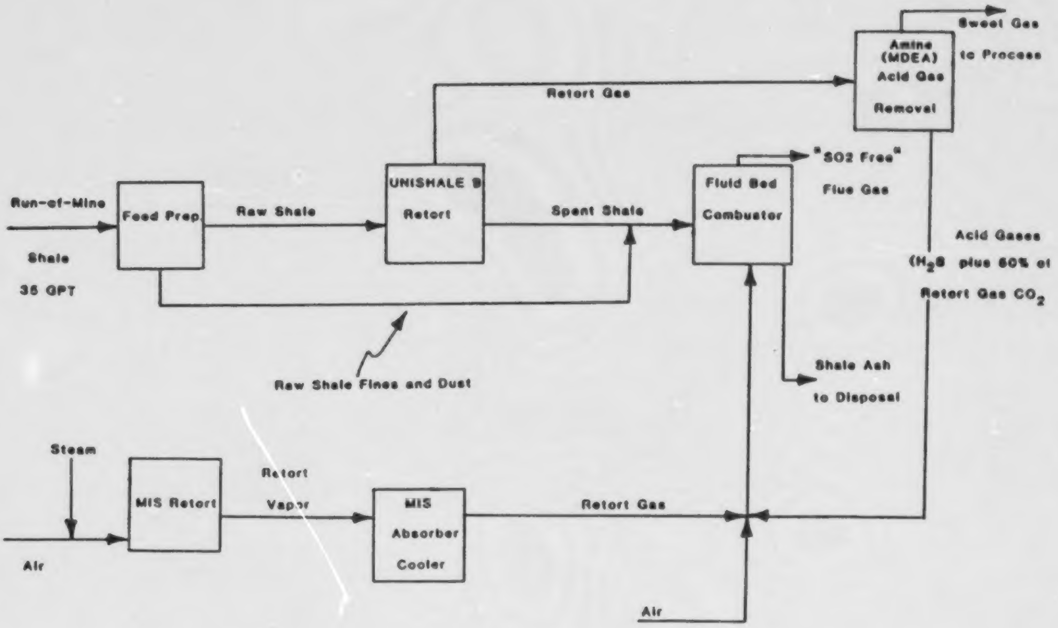
Sweet Gas
to Process
Amine
(MDEA)
Acid Gas
Removal
Retort Gas
"SO2 Free"
Flue Gas
Run-of-Mine
Shale
35 GPT
Feed Prep.
Raw Shale
UNISHALE B
Retort
Spent Shale
Fluid Bed
Combustor
Acid Gases
(H_2S plus 60% of
Retort Gas CO_2
Raw Shale Fines and Dust
Shale Ash
to Disposal
Steam
MIS Retort
Air
Retort
Vapor
MIS
Absorber
Cooler
Retort Gas
Air

FIGURE 4
PROCESS FLOW DIAGRAM FOR ASSP EVALUATION
DIRECT HEATED (MODIFIED IN-SITU WITH UNISHALE C)

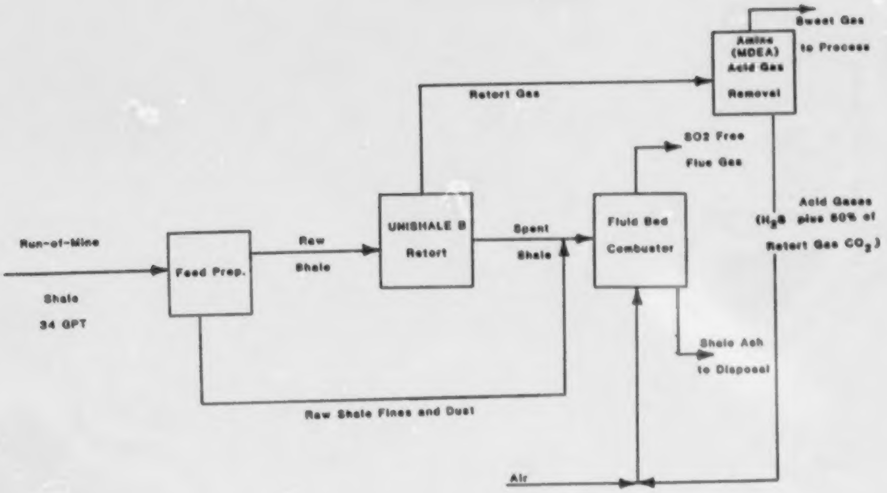
Run-of-Mine
Shale
34 GPT
Feed Prep.
Raw
Shale
UNISHALE B
Retort
Retort Gas
Amine
(MDEA)
Acid Gas
Removal
Sweet Gas
to Process
SO2 Free
Flue Gas
Spent
Shale
Fluid Bed
Combustor
Acid Gases
(H_2S plus 50% of
Retort Gas CO_2)
Shale Ash
to Disposal
Raw Shale Fines and Dust
Air

FIGURE 5

PROCESS FLOW DIAGRAM FOR ASSP EVALUATION
INDIRECT HEATED (UNISHALE B)

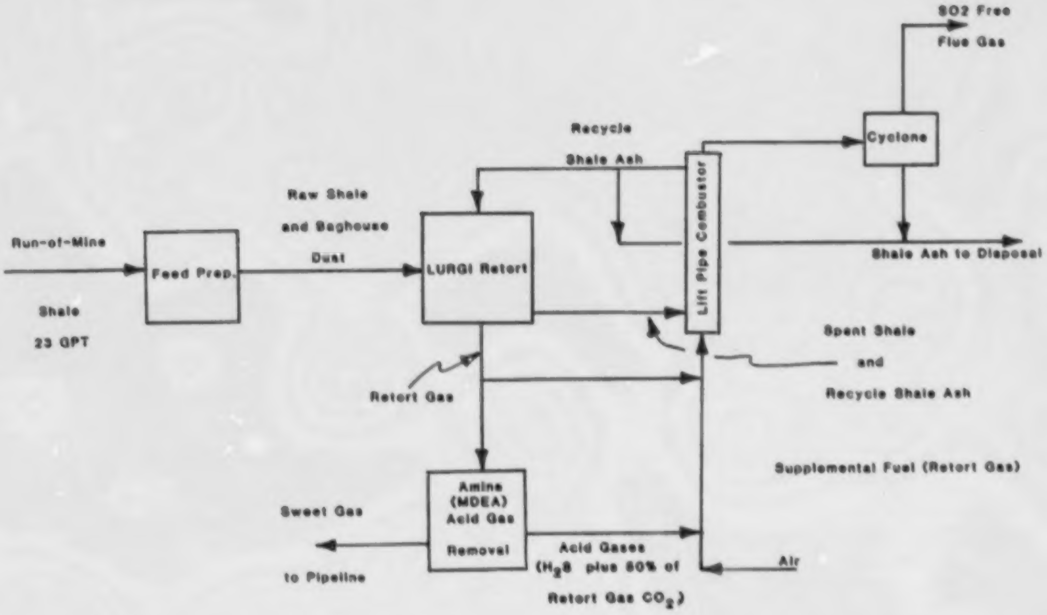
SO2 Free
Flue Gas
Recycle
Shale Ash
Cyclone
Raw Shale
and Baghouse
Dust
Run-of-Mine
Shale
23 GPT
Feed Prep.
LURGI Retort
Lift Pipe Combustor
Shale Ash to Disposal
Spent Shale
and
Recycle Shale Ash
Retort Gas
Supplemental Fuel (Retort Gas)
Sweet Gas
to Pipeline
Amine
(MDEA)
Acid Gas
Removal
Acid Gases
(H_2S plus 80% of
Retort Gas CO_2)
Air

FIGURE 6

PROCESS FLOW DIAGRAM FOR ASSP EVALUATION
INTEGRAL PART OF PROCESS (LURGI)

A separate study was done to select the best amine process for concentrating gases from Unishale B and Lurgi. Although the conventional sulfur control processes proposed for Unishale B and Lurgi retorting are the Unisulf and DEA/Stretford respectively, the methyldiethanolamine (MDEA) process was selected for ASSP because:

- It is partially selective for H_2S over CO_2. About 50% of the CO_2 will pass through, thus reducing solvent circulation requirements which in turn reduce both capital and operating costs.
- MDEA is not significantly degraded by COS.
- Hydrocarbon solubility is low.
- The process is non-proprietary.
- MDEA solvent is relatively inexpensive.
- No exotic metallurgy is required.

B. Costs

Equipment costs for Lurgi, Unishale B and C,, and MIS commercial plants were taken from the EPA Pollution Control Technical Manuals (PCTMs) which describe the Union(5), Cathedral Bluffs(1) (Tract C-b), and Rio Blanco(6) (Tract C-a) projects in detail. All major ASSP equipment items were sized and costs were factored from in-house data bases as well as information contained in the PCTMs. All cost data were factored to first quarter 1985 using the CE Plant Cost Index. Equipment additions and deletions are summarized in Table 2. Design bases for each retort type are summarized in Table 3. A summary of major equipment and process design parameters are given in Table 4.

TABLE 2. EQUIPMENT CHANGES FOR ASSP

<table>
<tr><th></th><th colspan="2">Direct Heated</th><th>Indirect</th><th colspan="2">Integral</th></tr>
<tr><th></th><th>Case A: FGD</th><th>Case B: Stretford</th><th>Heated</th><th colspan="2">Combustor</th></tr>
<tr><td>Retort Process</td><td>MIS/Unishale C</td><td>MIS/Unishale C</td><td>Unishale B</td><td>Lurgi</td><td>Unishale C</td></tr>
<tr><td>Systems Added for ASSP</td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td></td><td colspan="2">-------------MDEA--------------</td><td>MDEA</td><td>MDEA</td><td>MDEA</td></tr>
<tr><td></td><td colspan="2">--------Fluidized Beds---------</td><td>Fluidized Beds</td><td></td><td></td></tr>
<tr><td>Systems Deleted for ASSP</td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td></td><td>Unisulf
MIS FGD System
MIS Steam Boiler</td><td>Unisulf
MIS Stretford
MIS Steam Boiler</td><td>Unisulf
Recycle Gas Heater
Spent Shale Cooler</td><td>DEA
Stretford</td><td>Unisulf</td></tr>
</table>

Incremental capital costs for each ASSP case are summarized in Table 5. A summary of incremental annual operating costs is given in Table 6. Table 7 summarizes the incremental capital and operating costs for ASSP relative to the conventional sulfur removal schemes.

TABLE 3. CONCEPTUAL DESIGN BASES

	Direct Heated		Indirect Heated	Integral Combustor	
Retorting Process	MIS	Unishale C	Unishale B	Lurgi	Unishale C
Site	--Tract C-b--		Union	Tract C-a	Union
Plant Capacity, TPSD	36,200	13,600	27,200	119,000	27,200
Shale Grade, GPT	27	35	34	23	34
No. of Retorts	19	1	2	13	2
Conventional Sulfur Control: Case A:	FGD	Unisulf	Unisulf	DEA+ Stretford	Unisulf
Case B:	Stretford	Unisulf			
ASSP Parameters:					
Combustor Type	---Fluid Bed---		Fluid Bed	Lift Pipe	Fluid Bed
Number of Combustors	5		2	13	2
Temperature, °F	1350		1350	1200-1300	1350
Spent Shale Combusted, 10^3 lb/hr	871		1760	8533	1760
Raw Shale Combusted, 10^3 lb/hr	67		133	0	133
Retort Gases to Combustor, 10^3 lb/hr	1805		0	107	0
Acid Gases to Combustor, 10^3 lb/hr	12		11	29	11
Total Sulfur Fed to Combustor, lb/hr	5373		2204	1160	2204
Ca/S Molar Ratio	23		133	1088	133
Flue Gas SO_2, ppmv	10*		10*	30	10*

* Determined in Phase II Pilot Plant Program

TABLE 4. MAJOR PARAMETERS USED IN ASSP CONCEPTUAL DESIGNS

	Direct Heated		Indirect Heated	Integral Combustor	
Retorting Process	MIS	Unishale C	Unishale B	Lurgi	Unishale C
Site	-----Tract C-b------		Union	Tract C-a	Union
Number of Retorts	19	1	2	13	2
Raw Shale Grade, GPT	26.7	35	34	23	34
Raw Shale Processed, TPSD	36,200	13,600	27,200	119,000	27,200
Raw Shale Processed per Retort, TPSD	1,900	13,600	13,600	9,150	13,600
Net Oil Produced, BPSD	13,800	10,000	20,000	63,140	20,000
Net Retort Gas Produced, lb/hr	1,804,990	41,280	82,030	149,045	82,030
Sulfur Control Parameters (Base Case)					
Type of Sulfur Control	Case A: FGD Case B: Stretford	Case A: UNISULF Case B: UNISULF	UNISULF	DEA+ Stretford	UNISULF
Sulfur Produced, LTPSD	Case A: None Case B: 33.8	Case A: 19.5 Case B: 19.5	24.4	7.56	24.4
Spent Shale Combustion Parameters (Conceptual Designs)					
Type of Shale Combustor	NA	Fluid Bed	Fluid Bed	Lift Pipe	Fluid Bed
Number of Combustors	NA	5	2	13	2
Temperature, °F	NA	1350	1350	1200-1300	1350
Gas Residence Time, sec	1.0	1.0	1.0	1-3	1.0
Spent Shale Combusted, lb/hr	NA	870,607	1,759,250	8,533,105	1,759,250
Raw Shale Combusted, lb/hr	NA	66,666	133,333	0	133,333
Retort Gases to Combustors, lb/hr	1,804,990	0	0	107,028	0
Acid Gases to Combustors, lb/hr	0	11,905	11,304	28,675	11,304
Sulfur to Combustors, lb/hr	1,825	3,548	2,204	1,160	2,204
Ca/S Mole Ratio(a)	22.8	22.8	133	1,088	133
SO_2 in Combustor Flue Gas, ppmv	10	10	10	30	10

(a) Based on available calcium ($CaCO_3$ or CaO) in shales and total sulfur in retort gases and/or acid gases entering the spent shale combustor.

FGD = Flue Gas Desulfurization

NA = Not Applicable

TABLE 5. INCREMENTAL CAPITAL COST FOR ASSP CONCEPTUAL DESIGNS

	Direct Heated		Indirect Heated	Integral Combustor	
Retorting Process	MIS	Unishale C	Unishale B	Lurgi	Unishale C
Site	-----Tract C-b------		Union	Tract C-a	Union
Number of Retorts	19	1	2	13	2
Type of Spent Shale Combustors	NA	Fluidized Bed	Fluidized Bed	Lift Pipe	Fluidized Bed
Number of Combustors	NA	5	2	13	2
Added Capital Cost, $\$10^6$	Case A: MIS with FGD	Case B: MIS with Stretford			
MDEA Acid Gas Removal	$ 5.8	$ 5.8	$ 5.6	$ 9.9	$ 5.6
Lift Pipe Combustors	NA	NA	NA	No Charge	NA
Fluidized Bed Combustors	$ 130.0	$ 130.0	$ 146.0	NA	No Charge
TOTAL	$ 135.8	$ 135.8	$ 151.6	$ 9.9	$ 5.6
Deleted Capital Cost, $\$10^6$					
DEA Acid Gas Removal	NA	NA	NA	$(14.3)	NA
Stretford Sulfur Recovery	NA	$(48.0)	NA	$(8.6)	NA
UNISULF Sulfur Recovery	$(33.0)	$(33.0)	$(37.7)	NA	$(37.7)
Spent Shale Shaft Cooler	NA	NA	$(14.4)	NA	NA
Recycle Gas Heater	NA	NA	$(9.3)	NA	NA
Flue Gas Desulfurization	$(56.0)	NA	NA	NA	NA
MIS Gas Steam Boiler	$(118.0)	$(118.0)	NA	NA	NA
TOTAL	$(207.0)	$(199.0)	$(61.4)	$(22.9)	$(37.7)
Net Capital Cost (Credit), $\$10^6$	$(71.2)	$(63.2)	$ 90.2	$(13.0)	$(32.1)

FGD = Flue Gas Desulfurization
NA = Not Applicable

TABLE 6. INCREMENTAL OPERATING COSTS FOR ASSP CONCEPTUAL DESIGNS

	Direct Heated		Indirect Heated	Integral Combustor	
Retorting Process	MIS	Unishale C	Unishale B	Lurgi	Unishale C
Site	-----Tract C-b------		Union	Tract C-a	Union
Number of Retorts	19	1	2	13	2
Type of Spent Shale Combustor	NA	Fluidized Bed	Fluidized Bed	Lift Pipe	Fluidized Bed
Number of Combustors	NA	5	2	13	2
Added Operating Cost, $\$10^6$/Yr*	Case A: MIS with FGD	Case B: MIS with Stretford			
MDEA Acid Gas Removal	$ 1.26	$ 1.26	$ 1.24	$ 2.51	$ 1.24
Lift Pipe Combustors	NA	NA	NA	No Charge	NA
Fluidized Bed Combustors	$(16.66)	$(16.66)	$(4.54)	NA	No Charge
TOTAL	$(15.40)	$(15.40)	$(3.30)	$(2.51)	$ 1.24
Deleted Operating Cost, $\$10^6$/Yr*					
DEA Acid Gas Removal	NA	NA	NA	$(3.90)	NA
Stretford Sulfur Recovery	NA	$(5.97)	NA	$(0.90)	NA
UNISULF Sulfur Recovery	$(2.48)	$(2.48)	$(2.80)	NA	$(2.80)
Spent Shale Shaft Cooler and Recycle Gas Heater	NA	NA	$(13.11)	NA	NA
Flue Gas Desulfurization	($ 7.21)	NA	NA	NA	NA
MIS Gas Steam Boiler	$ 35.92	$ 35.92	NA	NA	NA
TOTAL	$ 26.23	$ 27.47	$(15.91)	$(4.80)	$(2.80)
Net Annual Operating Cost (Credit), $\$10^6$/Yr	$ 10.83	$ 12.07	$(19.21)	$(2.29)	$(1.56)

FGD = Flue Gas Desulfurization
NA = Not Applicable
* 150 psig steam $\$4.00/10^3$ lb
400 psig steam $\$4.50/10^3$ lb
600 psig steam $\$5.00/10^3$ lb
Fuel gas $\$3.00/10^6$ Btu
Electricity $0.05/kWh

TABLE 7. INCREMENTAL CAPITAL AND OPERATING COSTS FOR ASSP CONCEPTUAL DESIGNS

	Direct Heated		Indirect Heated	Integral Combustor	
Retorting Process	MIS	Unishale C	Unishale B	Lurgi	Unishale C
Site	-----Tract C-b------		Union	Tract C-a	Union
Number of Retorts	19	1	2	13	2
Type of Spent Shale Combustor	NA	Fluidized Bed(a)	Fluidized Bed(b)	Lift Pipe (c)	Fluidized Bed (d)
Number of Combustors	NA	5	2	13	2
Conceptual Design Summary	Case A: MIS w/FGD (e)	Case B: MIS w/Stretford (f)			
Systems Added for ASSP:	MDEA(g) -Fluidized Beds-(a)	MDEA	MDEA Fluidized Beds (b)	MDEA	MDEA
Systems Deleted for ASSP:	UNISULF(h) MIS FGD System MIS Steam Boiler	UNISULF MIS Stretford System MIS Steam Boiler	UNISULF Recycle Gas Heater Spent Shale Cooler	DEA(i) Stretford	UNISULF
Net Capital Cost (Credit), $\$10^6$	\$(71.2)	\$(63.2)	\$90.2	\$(13.0)	\$(32.1)
Net Annual Operating Cost, (Credit), $\$10^6$/yr	\$10.83	\$12.07	\$(19.21)	\$(2.29)	\$(1.56)

(a) Due to the large volume of MIS gases, five fluidized bed spent shale combustors are used with one Unishale retort.
(b) Each Unishale B retort requires one fluidized bed spent shale combustor.
(c) Each Lurgi retort contains one lift pipe spent shale combustor which has been integrated into the process.
(d) Each Unishale C retort contains a Unishale B retort plus a fluidized bed spent shale combustor which has been integrated into the process.
(e) FGD = Flue Gas Desulfurization using aqueous limestone scrubbers.
(f) Stretford = Holmes-Stretford sulfur recovery process.
(g) MDEA = Methyldiethanolamine acid gas removal unit.
(h) UNISULF = Union Oil proprietary sulfur recovery process.
(i) DEA = Diethanolamine acid gas removal unit.

Results of this study show that the best potential for application of ASSP are those processes which already have a spent shale combustor integrated into the retorting process (e.g., Lurgi, Unishale C, Chevron STB, and Tosco HSP). Capital and operating cost savings for Unishale C and Lurgi cases are primarily a result of deleting the Unisulf and Stretford plants.

For indirect heated processes (e.g., Paraho Indirect, Tosco II, and Unishale B), payout on the additional investment for ASSP equipment would be good to marginal depending primarily on how effectively the add-on spent shale combustor can be integrated into the process. That is, economically, it is better that heat from the combustor products be recovered and used directly in the retort rather than used for steam raising. For this study, it was assumed that combustor flue gases are used to heat recycle gas for the Union B retort (this has been proposed by Union as the preferred Unishale C scheme). The economics of this case are also quite sensitive to values used for steam and fuel. The values used here are considered quite conservative. Use of higher values will, of course, tilt the economics more favorably toward ASSP.

In the direct heated cases, results show substantial savings in capital costs for ASSP relative to both Stretford and flue gas desulfurization approaches. However, the capital savings are at the expense of increased operating costs primarily as a result of deleting the MIS steam boiler which produces much larger quantities of useable steam than can be produced by ASSP. Again, the economics here are quite sensitive to steam values, although, in this case, higher steam values would tilt the economics away from ASSP. Also, investment in fluid bed equipment is very large (on the order of $130 million) because of the very large volumes of dilute MIS retort gases which must be handled. However, if fast or circulating fluid beds can be utilized, the number of additional combustors required could be reduced from four to as few as one or two. This would reduce capital investment significantly and tilt the economics more in favor of ASSP.

There may also be an environmental advantage to using ASSP for the direct heated Case B. The ASSP process should remove the non-H_2S sulfur species from the MIS retort offgas, while the alternative Stretford process would not effectively remove the non-H_2S sulfur species.

IV. PILOT PLANT TESTING

A. Description of the Pilot Plant

The test facility used in Phase II was a pilot plant built by Tosco Corporation to develop their Hydrocarbon Solids Processing (HSP) process.(4) The pilot plant has a nominal capacity of six tons per day of oil shale and contains a fluidized bed combustor which is eighteen inches in diameter. A process flow diagram of the plant is shown in Figure 7. A description of the process is given below.

Raw oil shale, crushed to minus 1/4-inch and smaller, is pneumatically lifted to the shale feed weigh hopper system from which shale is metered into the retort at a constant rate. The raw shale from the weigh hopper can be preheated up to 300 to 500°F in the steam jacketed retort feed screw. The retort is an inclined rotating cylinder in which oil shale and hot heat carrier solids (from the fluid bed combustor) are mixed. The mixture of heat carrier and oil shale is conveyed concurrently through the retort to the retort accumulator. The feed rates of raw oil shale and heat carrier are adjusted to maintain the desired temperature in the retort, approximately 900°F.

The mixture of spent shale and heat carrier from the retort, called retorted solids, is pneumatically conveyed from the accumulator discharge screw into the fluid bed combustor using superheated steam. The fuel residue on the spent shale (primarily organic carbon and hydrogen) is combusted to provide part or all of the heat required to pyrolyze the oil shale. Combusted solids, which consititute the heat carrier, are drawn off from the fluid bed combustor and are recycled to the retort.

The combustor is an atmospheric, dense phase, bubbling, fluidized bed. The spent shale fuel is supplemented as needed by injection of natural gas or retort gas into the bed. Solid fuels such as raw oil shale and coal can also be used. The bed is fluidized by hot flue gases from an external burner. Flow rates of air, natural gas, retort gas and superheated steam are measured with orifice meters and controlled with pneumatic flow control valves. Flow rates are adjusted to maintain bed fluidization, bed temperature and oxygen concentration in the combustor flue gas. The dense phase bed level is indicated by a differential pressure measurement between the bottom of the bed and the top of the freeboard section. The dense phase bed density is measured by differential pressure measurement between the bottom of the bed and a point two feet above that point.

Flue gas and entrained shale ash from the combustor are cooled in a heat exchanger and the ash is separated from the flue gas in a baghouse. From this baghouse weigh bin the ash flows to a moisturizer where it is mixed with water prior to disposal. The clean flue gas flow is measured with an orifice meter prior to being vented to the atmosphere.

Pyrolysis vapors from the retort are cooled and the oil and water condensed in a quench tower and overhead condenser. Condensed heavy oil from the quench tower, as well as light oil and water condensed in the overhead condenser, are collected in separate drums. The non-condensed retort vapors are either

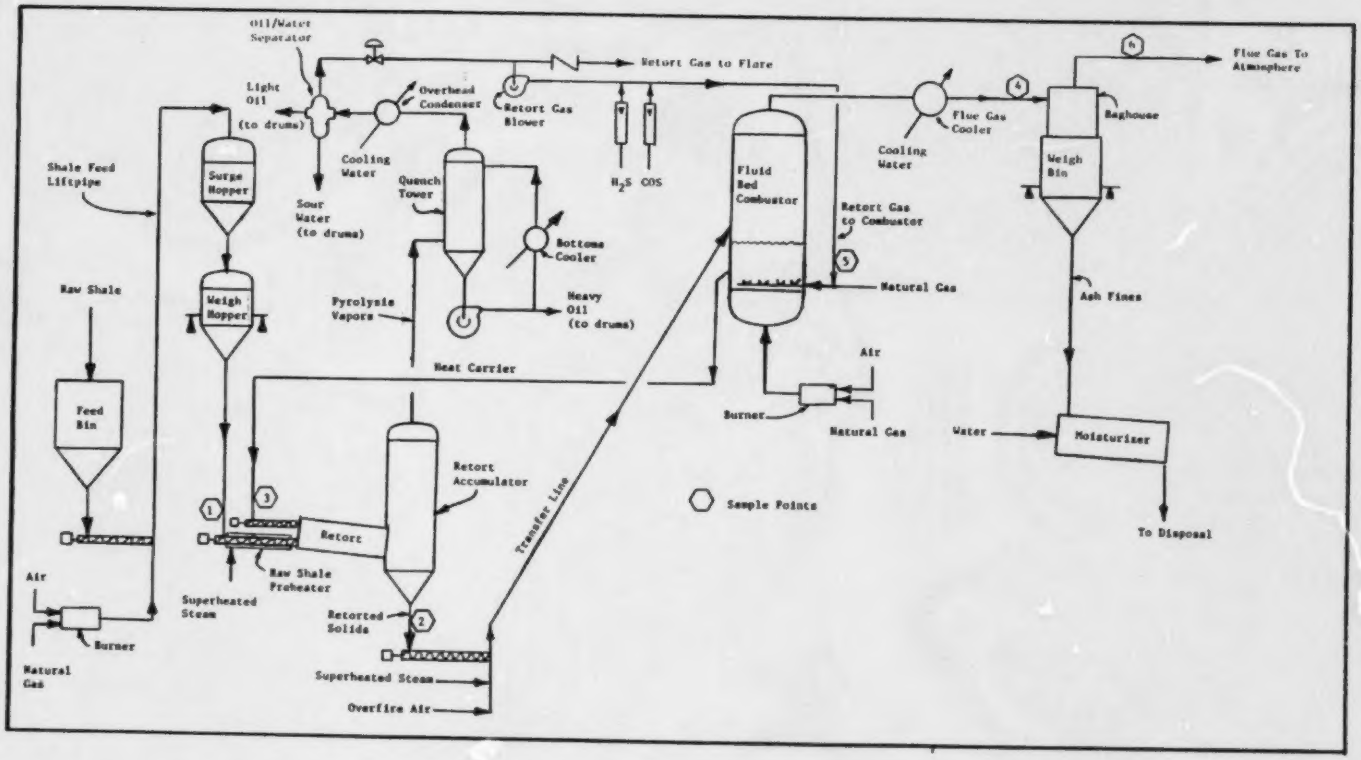
Oil/Water Separator
Light Oil (to drums)
Sour Water (to drums)
Cooling Water
Overhead Condenser
Retort Gas Blower
Retort Gas to Flare
H_2S
COS
Quench Tower
Bottoms Cooler
Heavy Oil (to drums)
Pyrolysis Vapors
Heat Carrier
Shale Feed Liftpipe
Surge Hopper
Weigh Hopper
Raw Shale
Feed Bin
Air
Burner
Natural Gas
1
3
Retort
Raw Shale Preheater
Superheated Steam
Retort Accumulator
Retorted Solids
2
Superheated Steam
Overfire Air
Transfer Line
Fluid Bed Combustor
Retort Gas to Combustor
5
Natural Gas
Air
Burner
Natural Gas
Sample Points
Cooling Water
Flue Gas Cooler
4
6
Flue Gas To Atmosphere
Baghouse
Weigh Bin
Ash Fines
Water
Moisturizer
To Disposal

FIGURE 7
PILOT PLANT PROCESS FLOW DIAGRAM

metered and sent to a flare or are diverted to the fluid bed combustor through a blower used to overcome the pressure in the bed. For the majority of the pilot plant tests, retort gas was burned in the fluid bed to supply the H_2S and non-H_2S sulfur compounds. In addition, H_2S and COS from pressurized cylinders was used to "spike" the retort gas to allow significantly higher sulfur concentrations in the injected retort gas than would have been possible with only retort gas.

B. Plant Instrumentation

In addition to instruments provided for process control, instrumentation was provided to determine mass flow balances around the fluid bed combustor and to monitor key component concentrations in the flue gas stream.

- Weights of raw shale feed and baghouse ash were continuously monitored by electronic weigh scale systems located on the respective hoppers.
- Mass flow rates of retorted solids and heat carrier were measured via calibrated screw conveyors.
- Combustor air, combustor burner natural gas, retort gas, transfer line superheated steam, transfer line air (overfire air used for secondary combustion) and combustor flue gas were all measured with orifice meters.
- Numerous air and nitrogen purges, used to keep pressure taps free of dust were individually measured by rotameters.
- Cylinder H_2S and COS injected into the retort gas were measured with rotameters.
- Sulfur content of the retort gas was continuously measured with an on-line sulfur analyzer.
- Concentrations of oxygen, carbon monoxide, nitrogen oxides and sulfur dioxide in the flue gas were continuously monitored via on-line analyzers.

C. Experimental Procedure

Parachute Creek oil shale obtained from the Colony mine was used for the pilot plant program. This shale was crushed to minus 1/4-inch particle size and had a nominal richness of 34-37 gallons per ton. Table 8 gives the analysis of two raw shale samples taken near the beginning and end of the pilot plant program. The shale used is similar to the shale being processed by the Union Oil commercial plant. This shale has significant amounts of calcium and magnesium carbonates, which when decomposed to the oxides, are available for sulfur absorption.

TABLE 8. PROPERTIES OF RAW SHALE USED IN COMBUSTOR TESTS

Test Number	7	19
Shale Size Range	1/4" x 0	1/4" x 0
Fischer Assay, GPT	36.9	34.2
Oil, wt %	13.9	12.9
Gas, wt %	2.5	2.5
Water, wt %	1.2	1.2
Residue, wt %	82.4	83.4
Moisture, wt%	0.73	1.49
Elemental Analysis, wt %		
Mineral Carbon	4.45	4.35
Organic Carbon	17.65	16.33
Hydrogen	2.35	2.24
Nitrogen	0.64	0.64
Sulfur	0.86	0.75
Ash Analysis, wt %		
Dolomite		
$MgCO_3$	11.4	8.9
$CaCO_3$	11.1	11.9
Total	22.5	20.8
Calcite		
CaCO3	12.5	13.8
Total $CaCO_3$	23.6	25.7
Ca, wt %	9.42	10.28
Mg, wt %	2.69	2.88
Screen Size, Standard Mesh, wt %		
+ 4	13.32	4.88
-4 + 8	49.66	38.82
-8 + 12	12.04	14.42
-12 + 20	12.02	17.06
-20 + 40	5.73	9.43
-40 + 80	3.63	6.76
-80	3.60	8.63

Some of the key process variables evaluated in the pilot plant program were:

- Bed temperature
- Solids residence time (bed depth and solids circulation rate)
- Gas residence time (superficial velocity)
- Ca/S mole ratio
- Flue gas oxygen concentration
- Raw shale/spent shale ratio
- Single stage and two stage combustion

During single stage combustion tests, all combustion air flows through the fluid bed and superheated steam is used to pneumatically convey retorted solids to the combustor via the transfer line. In this mode, the bed is normally oxygen-rich.

During two stage combustion tests, combustion air to the combustor is used as follows. First, combustion air to the bed is reduced until the flue gas oxygen concentration becomes zero. At this condition of running oxygen deficient in the bed, NO_x drops to minimum values and CO and trace hydrocarbons increase significantly. Then, overfire air is added to the retorted solids transfer line while simultaneously reducing superheated steam flow until the desired flue gas O_2 level is achieved. Since the transfer line does not enter the fluid bed, overfire air and superheated steam do not pass through the bed. Thus overfire air can only combust CO and trace hydrocarbons in the freeboard portion of the combustor. If done correctly, NO_x emissions theoretically should not increase as the overfire air is added to the combustor.

Bed temperature and solids residence time are the key variables that affect carbonate decomposition, a factor which is essential in obtaining efficient sulfur absorption. Because the combustor is integrated with the retort, none of the combustor operating conditions can be considered to be truly independent variables. That is, all operating conditions depend to some extent on other conditions:

- Combustor temperature depends upon:
  - Natural gas flow rate
  - Natural gas composition
  - Retort gas flow rate
  - Retort gas composition
  - Combustion air flow rate
  - Retorted solids flow rate
  - Retorted solids organic carbon content (which in turn depends on shale feed rate and retort temperature)
  - Temperatures of all streams entering the combustor.

- Retort temperature depends upon heat carrier rate, shale feed rate, and their respective temperatures.

- Solids residence time depends upon:
  - Retorted solids flow rate
  - Combustor bed depth

- Gas residence time depends upon:
  - Gas superficial velocity in the bed
  - Combustor bed depth

- Superficial gas velocity depends upon:
  - Combustion air flow rate
  - Natural gas flow rate
  - Retort gas flow rate

- Ca/S mole ratio depends upon:
  - Retort gas flow rate
  - Retort gas sulfur concentration
  - Retorted solids flow rate and calcium concentration

- Flue gas oxygen concentration depends upon:
  - Combustion air flow rate
  - Natural gas flow rate and composition
  - Retort gas flow rate and composition
  - Retorted solids flow rate and organic carbon concentration
  - Combustion efficiency
  - Carbonate decomposition

Since superheated steam was used to pneumatically convey retorted solids to the combustor, the steam flow rate will affect the wet flue gas composition, but will not affect the dry flue gas composition. Also, since the steam discharges solids near the top of the bed and not into the bed, the steam does not pass through the bed and so does not affect gas superficial velocity or cause dilution of the gases in the bed.

Due to the interdependence of one variable on another, a parametic study where one condition at a time is varied while holding all other conditions constant was not possible.

Because a large number of tests were planned to evaluate the effect of process variables on SO_2 and NO_x emissions, complete material balances were not possible in the two week operating period. Instead, mass flow balances were done on 44 "tests". A test consisted of the following: After the pilot plant was started up and was run at steady state conditions for 1-2 hours, a test was officially started. Operating data on all streams in and out of the combustor were taken. Such data included temperatures, pressures, orifice and rotameter readings for the retorted solids and heat carrier screw RPM's, and mass flow rates calculated from the change in the raw shale and baghouse ash weigh hopper readings. In addition, oxygen, carbon monoxide, SO_2 and NO_x readings on the four flue gas on-stream analyzers were recorded along with the sulfur concentration from the retort gas on-line analyzer. While these data were being taken, samples of raw shale, retorted solids, heat carrier, baghouse ash, retort gas and combustor flue gas were also taken. A description of the sampling procedures used for these tests is given in Section VI, as well as the analytical methods used on the samples.

Recording the test operating data and obtaining the six samples would normally take about 15 to 20 minutes. When all data and samples for a test were acquired, operating conditions were changed and the pilot plant and combustor allowed to line out at a new set of conditions. When the combustor was lined out on these new conditions for 1-2 hours, a new test would start with the taking of data and samples.

While operating data was logged for each of the 44 tests, solid and gas samples were taken on only 27 of these tests as shown in Table A-1. Twenty tests were selected for more complete evaluation by submitting the solids samples for chemical analysis. Eight of these twenty tests were analyzed fairly completely and the other 12 were subjected to a more routine analysis. The solids and gases from three tests were analyzed for six trace elements (arsenic, cadmium, mercury, beryllium, lead and fluoride). Large (5-gallon) samples of baghouse ash were also collected during three other tests for leaching studies at Colorado State University.

D. Discussion of Results

Key operating conditions for the 44 tests performed are given in Table A-2. The range of operating conditions and process variables for these tests are summarized below:

TABLE 9. RANGE OF OPERATING CONDITIONS AND PROCESS VARIABLES

Bed Temperature, °F	1127-1558
Freeboard Temperature, °F	1273-1593
Bed Pressure, Inches of Water	66- 102
Retorted Solids to Combustor, lb/hr	2487-3615
Raw Shale to Combustor, lb/hr	0- 133
Retort Gas to Combustor, SCFM	0-6.66
H_2S in Retort Gas, mole %	0.43-9.28
Bed Depth, ft	3.27-4.28
Solids Residence Time, min.	8.07-18.72
Gas Superficial Velocity, ft/sec	3.78-7.20
Gas Residence Time, sec	0.46-1.13
Flue Gas Oxygen, mole %	0-6.25
Carbonate Decomposition, %	45.5-83.3
Ca/S Mole Ratio	6.20-10.25

Over this range of conditions, flue gas composition and organic carbon combustion efficiency ranged as follows:

TABLE 10. RANGE OF FLUE GAS COMPOSITION AND ORGANIC CARBON COMBUSTION EFFICIENCY

Flue Gas Composition	Range
SO_2, ppmv	1-38
NO_x, ppmv	80-670
CO, mole %	0.05-1.80
Trace Hydrocarbons, ppmv	51-8465
Organic Carbon Combustion Efficiency %	57.5-100.0

Solid samples from 20 tests were analyzed for total carbon, mineral (carbonate) carbon, hydrogen, nitrogen and sulfur. Organic carbon was calculated by subtracting mineral carbon from total carbon. On eight of these 20 tests, dolomite [$CaMg(CO_3)_2$], calcite ($CaCO_3$) and calcium and magnesium contents were determined, as well as particle size analysis. Analyses of retorted solids, heat carrier and baghouse ash are given in Tables A-3, A-4 and A-5.

Analysis of selected solids from Tests 7, 12 and 19 by X-ray fluorescence is shown in Table A-6. The weight percent of fourteen elements is defined by this analysis.

The range of composition for these solids is summarized below:

TABLE 11. RANGE OF SOLIDS COMPOSITION

	Retorted Solids	Heat Carrier	Baghouse Ash
Mineral Carbon, wt%	0.58 - 1.63	0.32 - 1.45	0.76 - 4.72
Organic Carbon, wt%	0.37 - 0.97	0.00 - 0.30	0.00 - 1.53
Hydrogen, wt%	0.01 - 0.13	0.00 - 0.06	0.00 - 0.24
Nitrogen, wt%	0.04 - 0.15	0.00 - 0.12	0.09 - 0.33
Sulfur, wt%	0.38 - 0.86	0.41 - 0.84	0.99 - 1.81
Dolomite			
$MgCO_3$, wt%	0.0 - 0.0	0.0 - 0.0	0.0 - 5.8
$CaCO_3$, wt %	0.0 - 3.7	0.0 - 1.6	0.0 - 15.2
Calcite ($CaCO_3$), wt%	4.8 - 9.8	2.8 - 9.4	6.3 - 19.5
Total $CaCO_3$, wt%	4.8 - 13.1	2.8 - 11.0	6.3 - 32.4
Ca, wt%	4.87 - 7.00	4.60 - 7.23	13.00 - 16.50
Mg, wt%	1.37 - 1.86	1.28 - 1.97	3.70 - 4.48

In general, the particle size range of the retorted solids and heat carrier did not exhibit significant differences, probably because the heat carrier comprised about 85% of the retorted solids mass. The baghouse ash, however, was primarily -80 mesh material, with a mean diameter of 7.9 to 10.4 microns. A particle size analysis of the -80 mesh fraction of the baghouse ash is also given in Table A-5.

Natural gas and retort gas were used to supply part of the combustor heat. Analyses of these gases is given in Table A-7. Only one natural gas analysis was taken since in the past the composition of this gas has been fairly stable.

Retort gas contained from 23 to 58 percent nitrogen due to the use of nitrogen purges around the retort. On two tests (9 and 15), retort gas became diluted with air when the blower used to feed retort gas to the combustor developed a negative suction pressure and air was drawn into the retort gas system. During these tests, oxygen and nitrogen comprised 78 to 86 percent of the gas.

To increase the sulfur concentration in the retort gas, H_2S and COS from pressurized cylinders were injected into the retort gas upstream of the sampling point. This increased the H_2S concentration from an initial concentration of about 0.4 - 0.5 mole percent to 2 - 4 percent and in Test 8, 9.3 percent. The retort gas was spiked with H_2S and COS in 33 of the 44 tests.

A continuous sulfur analyzer was also used on the retort gas. However this analyzer did not perform consistently, and although it was calibrated once or more each day, it tended to drift out of calibration quickly. Therefore, data from this analyzer is considered unreliable and is not used in any of the correlations. Data obtained from gas bomb samples was used instead.

Flue gas from the combustor was analyzed continuously for oxygen, carbon monoxide, sulfur dioxide and nitrogen oxides. These analyses are given in Table A-8 along with gas chromatographic (GC) analyses.

Flue gas samples were also analyzed for trace hydrocarbons using a GC/flame ionization detector.

To calculate the flue gas mass flow rate, the molecular weight of the wet flue gas was needed. Since the dry flue gas mole weight was available from GC analysis, the moisture content of the flue gas was estimated using nitrogen as a tie element.

For those tests where flue gas GC analyses were not available, dry flue gas nitrogen content and molecular weight values were estimated from tests with similar operating conditions.

Mass flow rate balances for all 44 tests are given in Table A-9. Each stream was calculated or estimated as follows:

TABLE 12. MASS FLOW RATE MEASUREMENTS

Stream	How Measured or Estimated
Raw Shale to Retort	Weigh Hopper
Heat Carrier	Calibrated Screw
Retorted Solids	Heat Carrier Rate + (0.82 x Raw Shale Rate)
Baghouse Ash	Weigh Hopper
Combustion Air	Orifice
Natural Gas	Orifice
Retort Gas	Orifice
Overfire Air	Orifice
Superheated Steam	Orifice
Raw Shale to Combustor	Calibrated Screw
Air/N_2 Purges	Rotameters
H_2S/COS injected into Retort Gas	Rotameters
Wet Flue Gas	Estimated from Orifice and Dry Flue Gas Analysis

Initially, it was planned to measure retorted solids flow by a calibrated screw, but due to the variable flow characteristics of this stream it was almost impossible to get a reliable flow rate determination. Therefore, it was decided to take the heat carrier rate, which was fairly constant during a given test and add to that the estimated spent shale production rate (0.82 x raw shale rate) to get the retorted solids flow rate.

In general, mass flow balances for all 44 tests were fairly good, as seen in Table A-9. The balance closure averaged 98.63 percent. For the 20 tests subjected to solids analysis the balance closure averaged 98.35 percent.

Total carbon, mineral carbon, organic carbon and sulfur balances were calculated for 20 tests using the mass flow rates from Table A-9, the elemental analyses for raw shale, retorted solids, heat carrier and baghouse ash and the natural gas, retort gas and flue gas compositions. The total carbon, mineral carbon and organic carbon balances are given in Tables A-10, A-11 and A-12, respectively. Mineral carbon balances were forced to 100 percent closure by adjusting the mineral carbon in the flue gas. Total carbon balances had an average balance closure of 108.95 percent, and organic carbon balances had an average closure of 115.41 percent.

Sulfur balances for the 20 selected tests are given in Table A-13. Essentially no sulfur was found in the flue gas. Sulfur in the baghouse ash was fairly constant while sulfur in the heat carrier varied in a manner similar to the retorted solids. Sulfur balance closure averaged 105.17 percent.

Nitrogen accountability in the solid streams and as flue gas NO_x is shown in Table A-14. Only nitrogen in the solids and in NO_x was considered, since consideration of elemental nitrogen in the gas streams would have overshadowed the nitrogen in the solid streams and flue gas NO_x by several orders of magnitude. These tests showed that nitrogen in the feed converted to NO_x varied from 0.6 to 19.2 percent, with an average conversion of 6.0 percent.

E. Process Variable Correlations

The extent to which process variables correlated with SO_2, NO_x, CO and trace hydrocarbon emissions as well as to organic carbon combustion efficiency is summarized in Table 13. Decreasing oxygen concentration in the flue gas tended to increase SO_2 emissions. Figure 8 shows the effect of analyzer O_2 on flue gas SO_2. Tests where both raw and spent shale were fed to the combustor showed the highest SO_2 levels. No difference was seen between single stage and two stage combustion, however.

Decreasing oxygen concentration tends to decrease NO_x emissions, as shown in Figure 9. Staged combustion did not show a reduction in NO_x emissions over single stage combustion as had been expected.

This unexpected result may be due to the burning of fines in the oxygen-rich freeboard generating significant quantities of NO_x. Some points to consider are:

- The nitrogen rich fines (baghouse ash) contain an average of 27 percent of the nitrogen in the solids fed to the combustor even though the fines only account for 15 percent of the retorted solids fed.
- Higher temperatures in the freeboard due to the burning of fines (up to 300°F higher) would mean greater reactivity of the fines.
- The smaller particle size of the fines could result in increased combustion rates.
- Gas residence times in the freeboard can be two to three times the gas residence time in the bed.
- The freeboard generally contains some excess oxygen, and as seen in Figure 9, NO_x tends to increase as oxygen concentration increases.

Decreasing oxygen concentration increased CO emissions as shown in Figure 10. As oxygen concentration nears zero percent, CO levels increase dramatically.

TABLE 13. PROCESS VARIABLE CORRELATIONS

Variables Which Produced A Correlation

GC O_2	versus	Flue Gas SO_2
Analyzer O_2	versus	Flue Gas SO_2
GC O_2	versus	Flue Gas NO_x
Analyzer O_2	versus	Flue Gas NO_x
GC O_2	versus	Flue Gas CO
Analyzer O_2	versus	Flue Gas CO
GC O_2	versus	Flue Gas Trace Hydrocarbons
GC O_2	versus	Baghouse Ash Organic Carbon
Solids Residence Time	versus	Flue Gas SO_2
Solids Residence Time	versus	Flue Gas NO_x
Solids Residence Time	versus	Flue Gas CO
Bed Organic Carbon	versus	Organic Carbon Combustion Efficiency
Ash Organic Carbon	versus	Organic Carbon Combustion Efficiency
Flue Gas CO	versus	Flue Gas NO_x
Flue Gas SO_2	versus	Flue Gas NO_x

Variables Which Did Not Produce A Correlation

GC O_2	versus	Organic Carbon Combustion Efficiency
Bed Organic Carbon	versus	Flue Gas NO_x
Ash Organic Carbon	versus	Flue Gas NO_x
Solids Residence Time	versus	Organic Carbon Combustion Efficiency
Gas Residence Time	versus	Flue Gas SO_2
Gas Residence Time	versus	Flue Gas NO_x
Gas Residence Time	versus	Flue Gas CO
Gas Residence Time	versus	Organic Carbon Combustion Efficiency
Fluid Bed Temperature	versus	Flue Gas SO_2
Fluid Bed Temperature	versus	Flue Gas NO_x
Fluid Bed Temperature	versus	Flue Gas CO
Fluid Bed Temperature	versus	Organic Carbon Combustion Efficiency
Ca/S Mole Ratio	versus	Flue Gas SO_2
C/N Mole Ratio	versus	Flue Gas NO_x

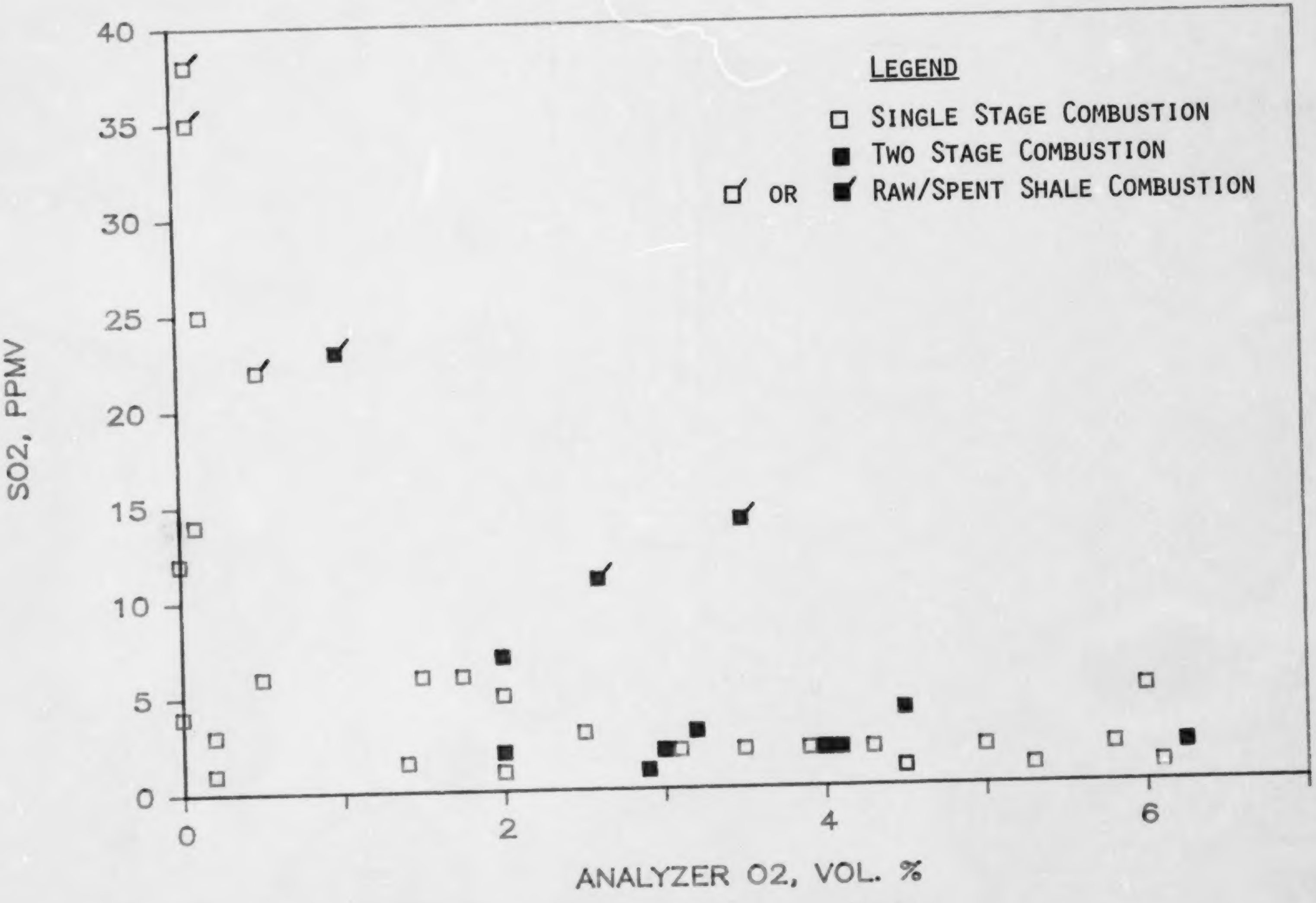

FIGURE 8. EFFECT OF FLUE GAS OXYGEN ON SO_2 EMISSIONS.

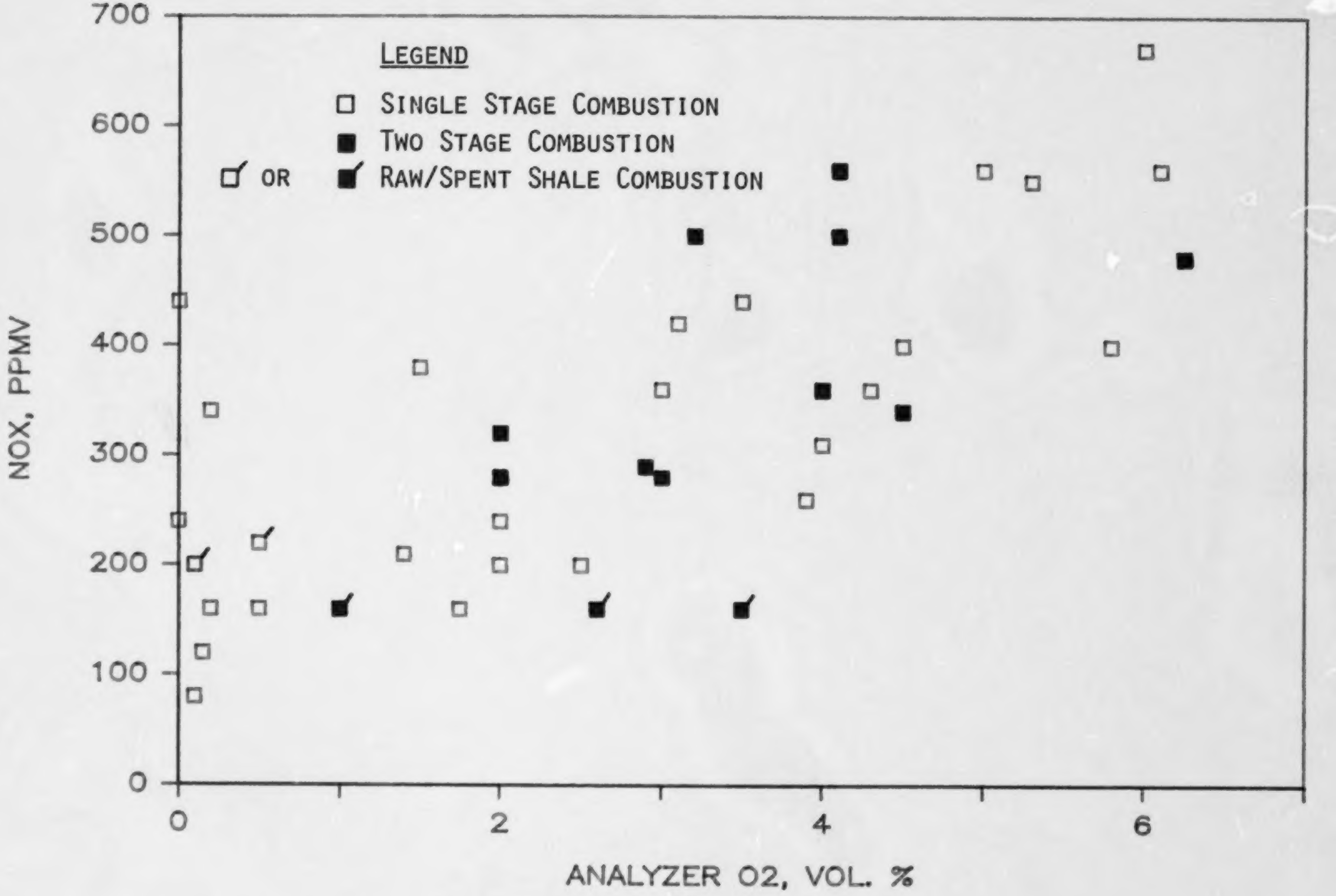

FIGURE 9. EFFECT OF FLUE GAS OXYGEN ON NO_X EMISSIONS.

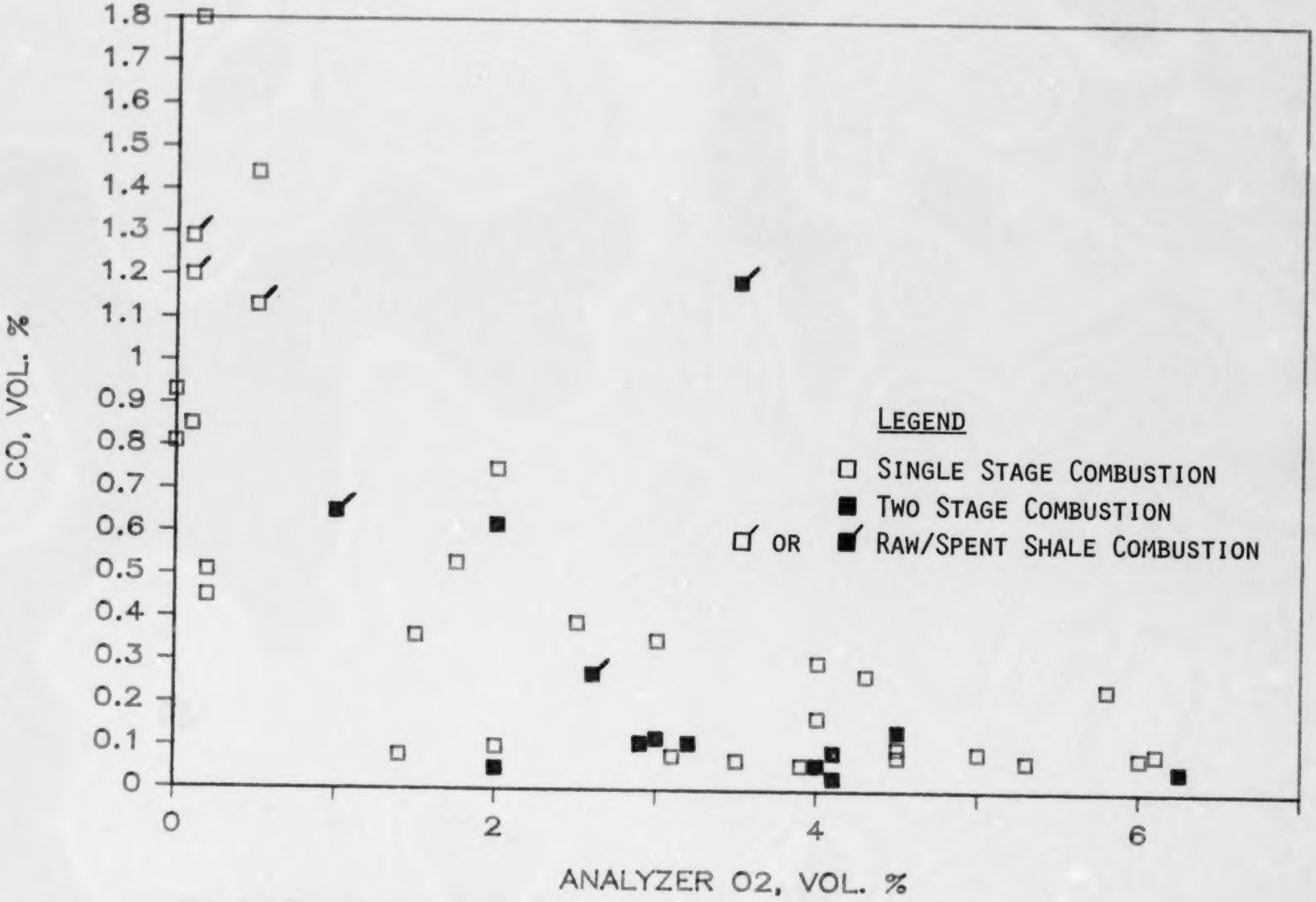

FIGURE 10. EFFECT OF FLUE GAS OXYGEN ON CO EMISSIONS.

The effect of oxygen concentration on trace hydrocarbons is shown in Figure 11. Trace hydrocarbons also increase dramatically as oxygen concentration approaches zero.

As oxygen concentration decreases below two percent, SO_2, CO, and trace hydrocarbon emissions increase significantly. Thus, two percent O_2 is felt to be a minimum for controlling these emissions from a spent shale combustor.

Decreasing oxygen concentration also tends to increase the organic carbon content of the baghouse ash, as shown in Figure 12. However, oxygen concentration did not correlate with organic carbon combustion efficiency.

As the solids residence time in the combustor decreases, SO_2 emissions increase (Figure 13), NO_x emissions tend to decrease (Figure 14) and CO emissions tend to increase (Figure 15). Although there is considerable scatter in the NO_x and CO data, general trends are apparent. Solids residence time did not correlate with organic carbon combustion efficiency.

Neither gas residence time nor bed temperature correlated with SO_2, NO_x, CO or organic carbon combustion efficiency. The scatter in the plot of fluid bed temperature vs. SO_2 emissions is shown in Figure 16.

Dependent variables which were found to correlate are bed organic carbon vs. organic carbon combustion efficiency (Figure 17) and baghouse ash organic carbon vs. organic carbon combustion efficiency (Figure 18). However, these correlations would be expected since organic carbon contents of both solids streams used to calculate organic carbon combustion efficiency. The ash organic carbon vs. combustion efficiency (Figure 18) shows two separate correlations, one for single stage combustion and one for two stage combustion. Other dependent variables that could be cross-correlated were CO vs. NO_x and SO_2 vs. NO_x.

At the high Ca/S ratios studied in this program, no effect was seen on SO_2 emissions over the range of 6.2 to 10.2 Ca/S mole ratio. It is speculated that at low ratios an increase in SO_2 emissions might be observed.

Increasing the organic carbon/nitrogen ratio in the fluid bed would be expected to decrease NO_x emissions. No such correlation was found, however.

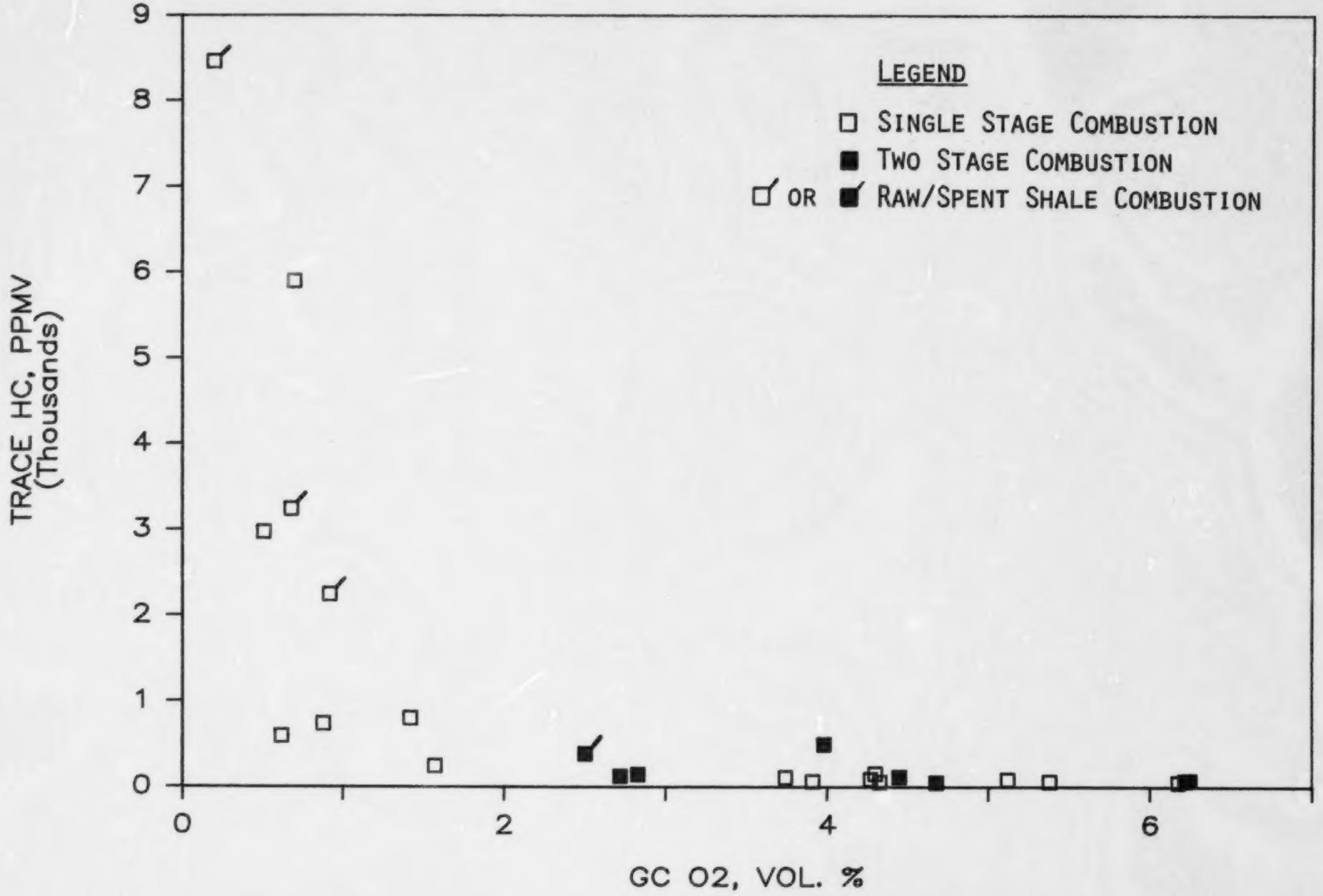

FIGURE 11. EFFECT OF FLUE GAS OXYGEN ON TRACE HYDROCARBON EMISSIONS.

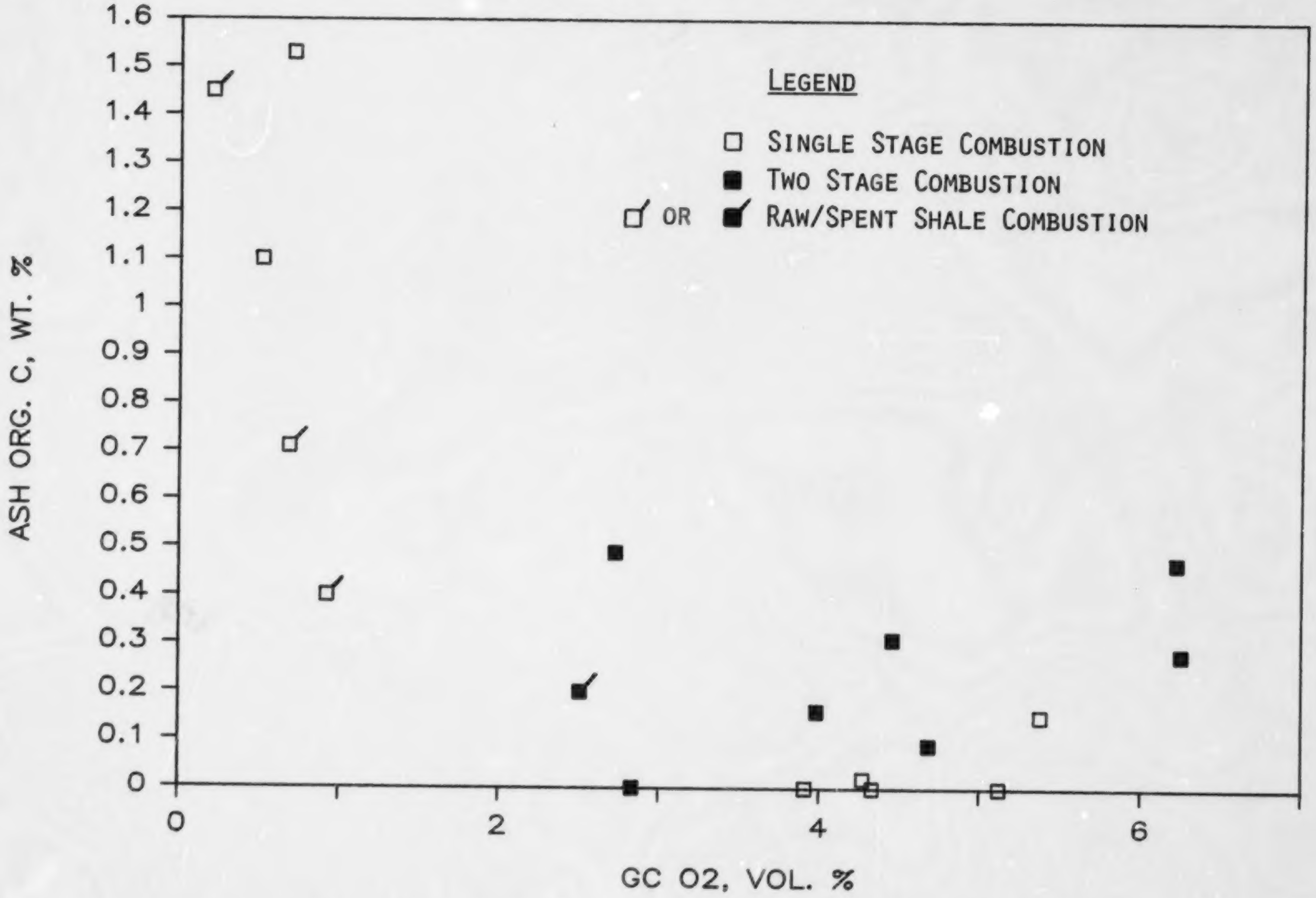

FIGURE 12. EFFECT OF FLUE GAS OXYGEN ON BAGHOUSE ASH ORGANIC CARBON.

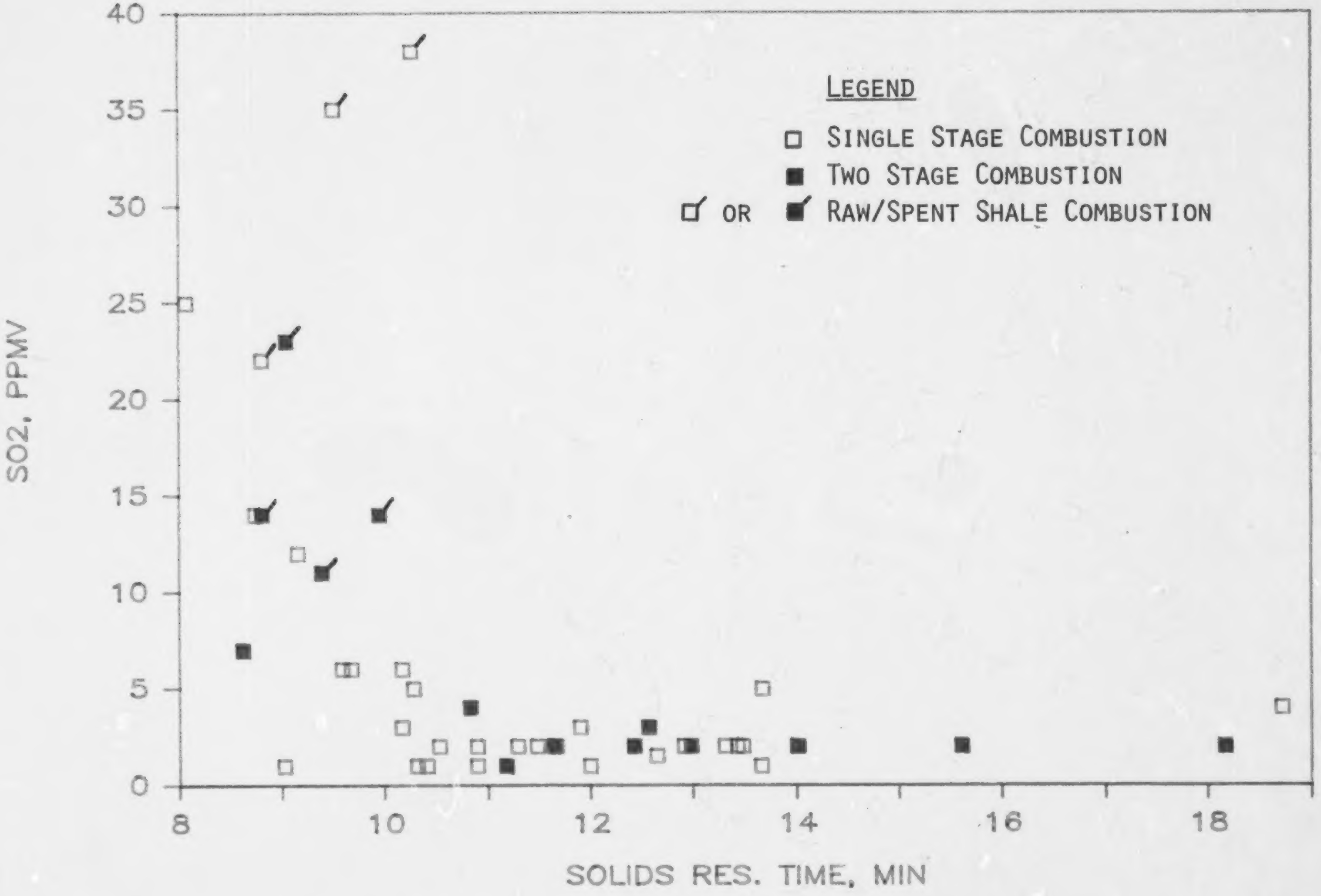

FIGURE 13. EFFECT OF SOLIDS RESIDENCE TIME ON SO_2 EMISSIONS.

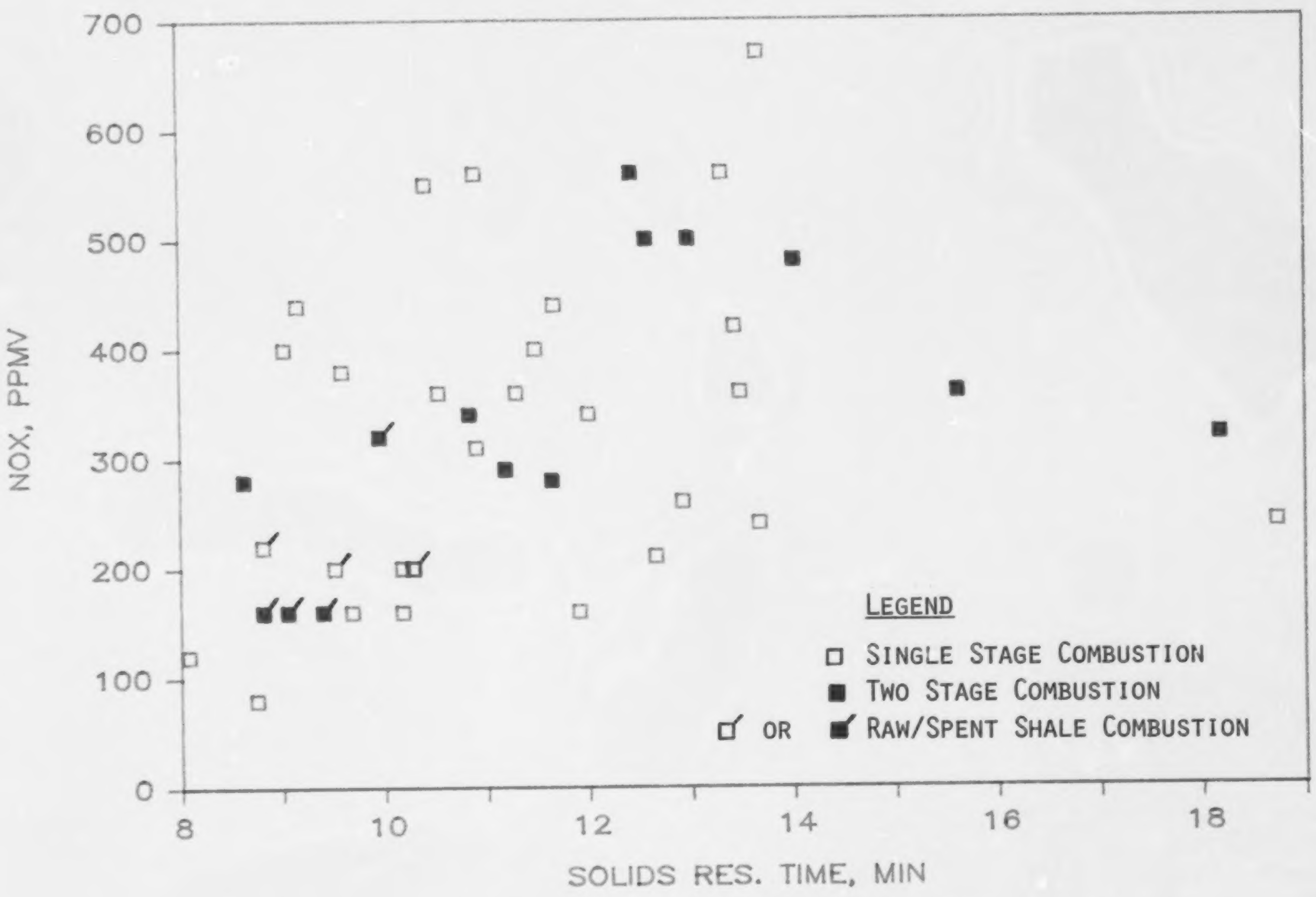

FIGURE 14. EFFECT OF SOLIDS RESIDENCE TIME ON NO_X EMISSIONS.

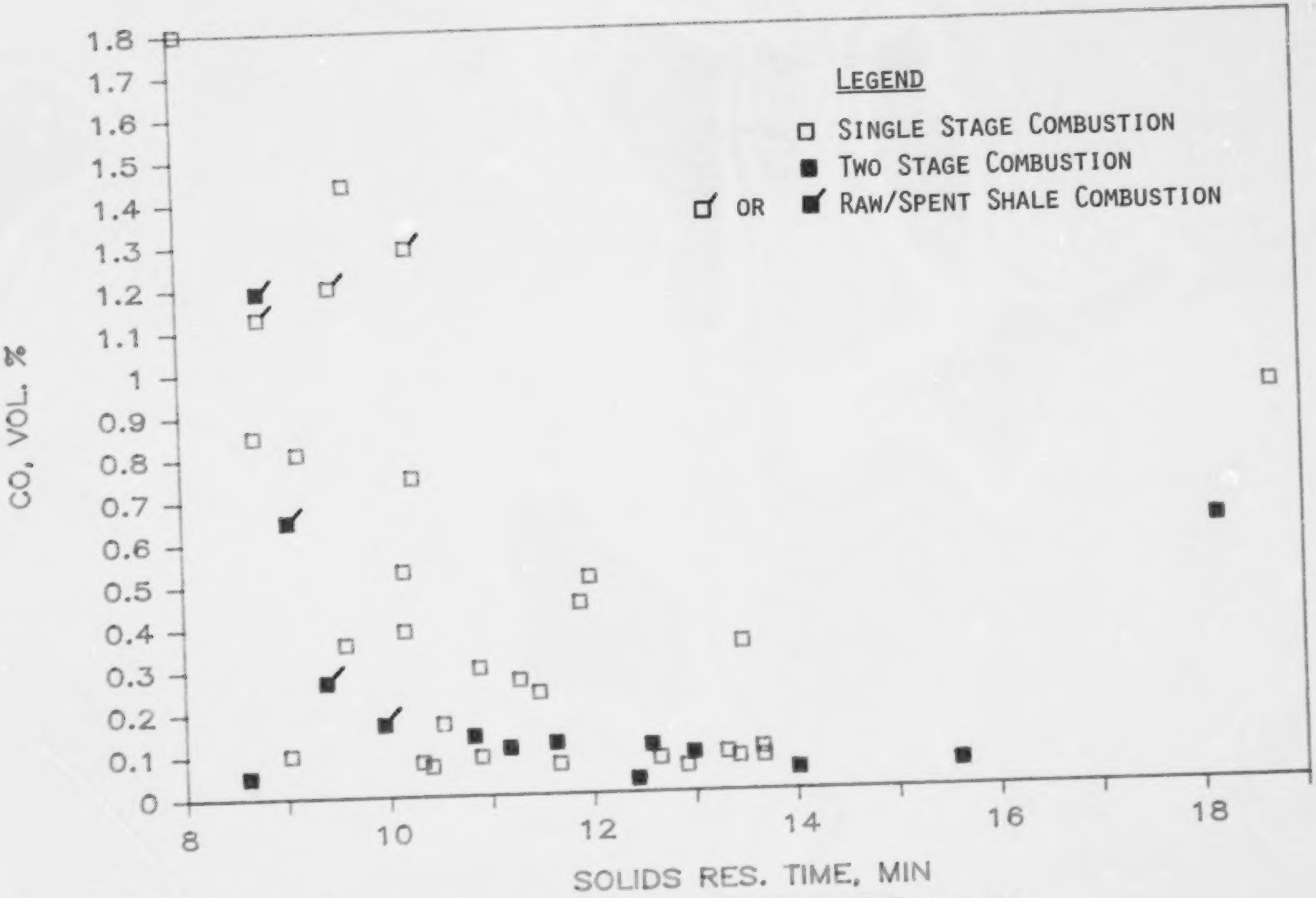

FIGURE 15. EFFECT OF SOLIDS RESIDENCE TIME ON CO EMISSIONS.

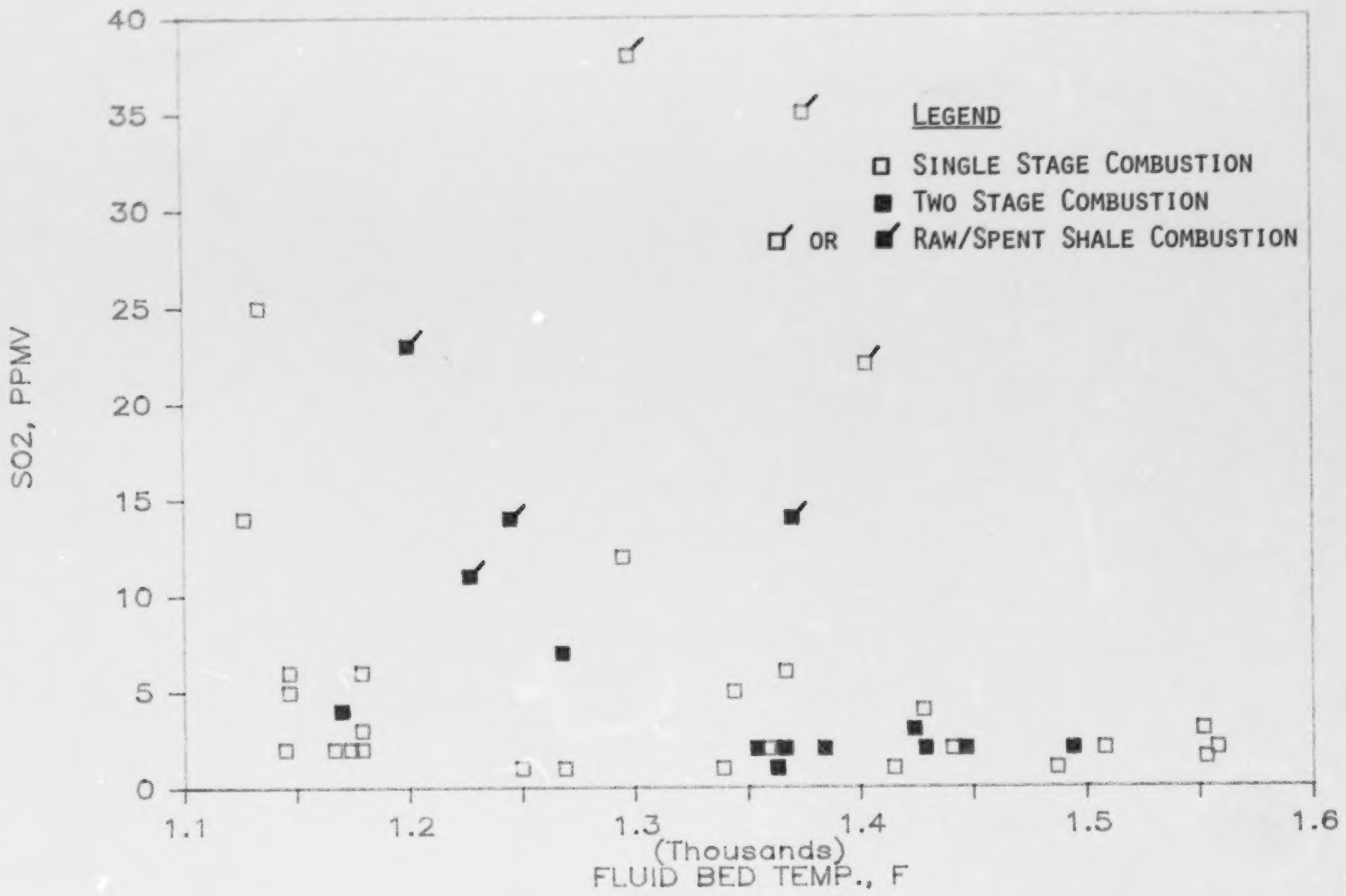

FIGURE 16. EFFECT OF FLUID BED TEMPERATURE ON SO_2 EMISSIONS.

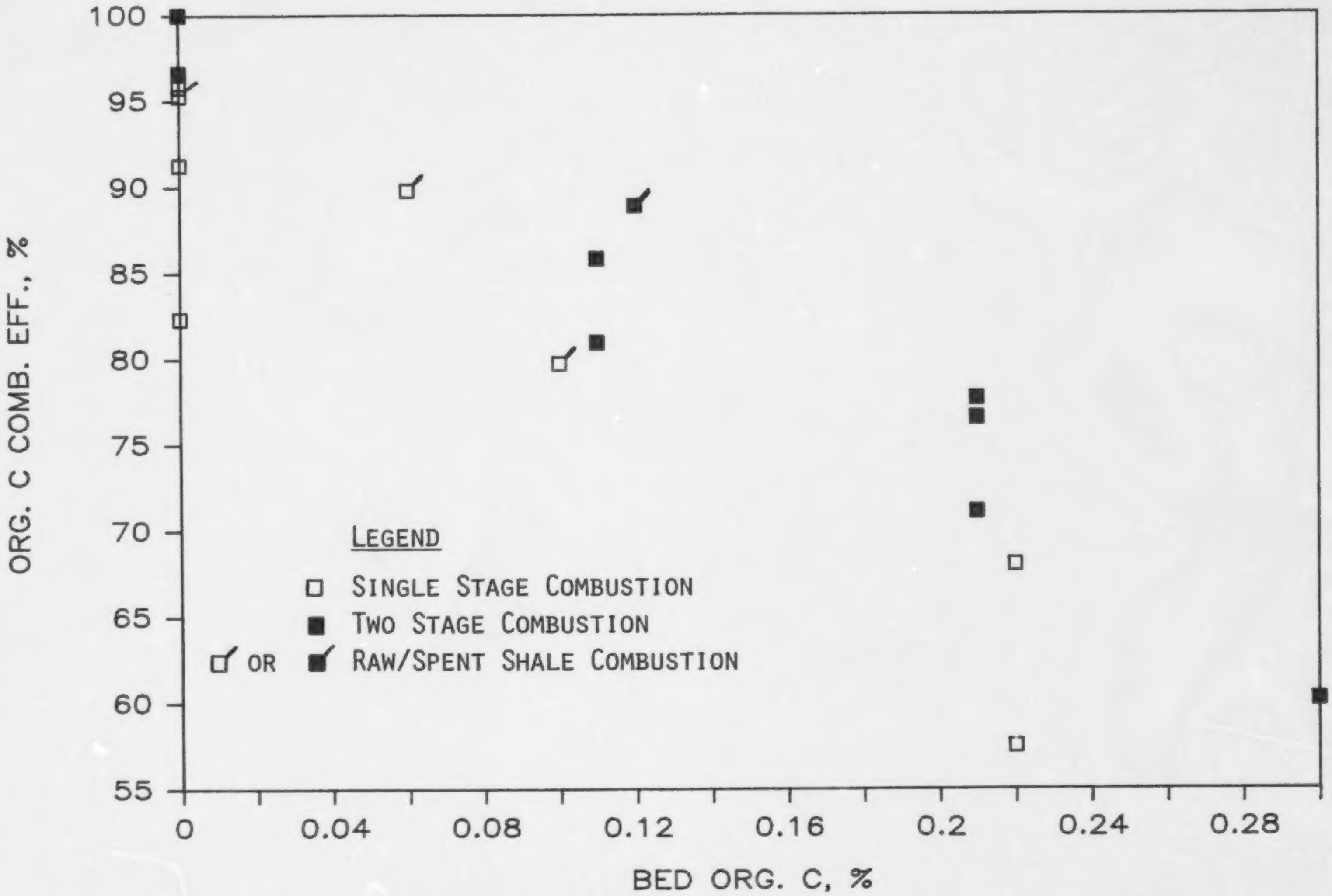

FIGURE 17. EFFECT OF FLUID BED ORGANIC CARBON ON ORGANIC CARBON COMBUSTION EFFICIENCY.

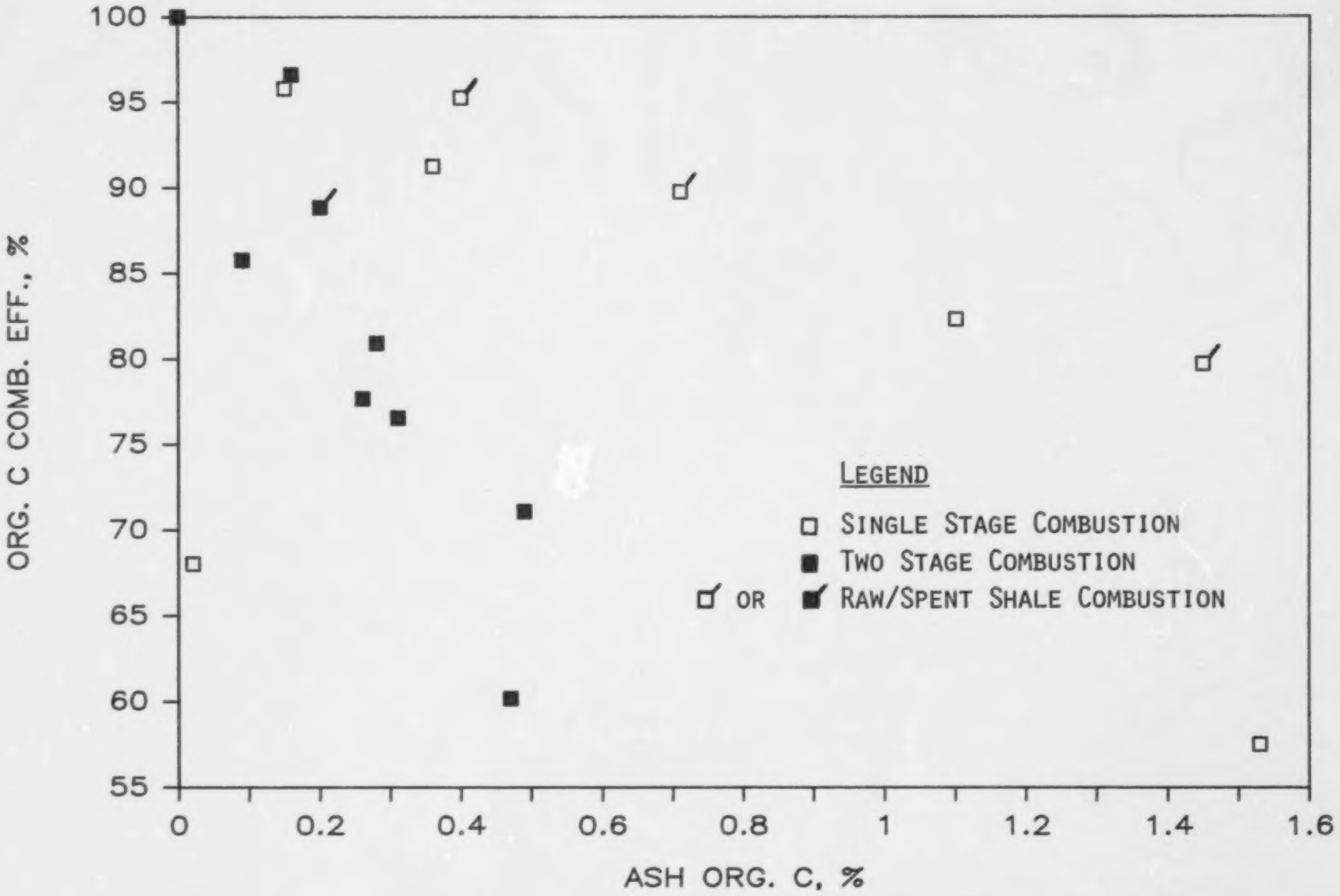

FIGURE 18. EFFECT OF BAGHOUSE ASH ORGANIC CARBON ON ORGANIC CARBON COMBUSTION EFFICIENCY.

F. Trace Element Sampling and Analyses

This section describes and discusses the sampling and analyses of selected process streams for the following trace elements: arsenic, cadmium, mercury, beryllium, lead and fluorine as fluoride. The streams sampled and analyzed were raw shale, retorted solids, heat carrier, baghouse ash, retort gas and combustor flue gas. Oil and retort water were not analyzed. The primary goal was to determine the trace element concentration in the retort gas and flue gas.

Previous investigators (7-18) have measured trace element concentrations in various process streams from laboratory and simulated in-situ retorts. Mercury concentrations of from less than 0.2 to 8,200 ug/m^3 have been reported in retort gases. Cadmium concentrations of from 1 ug/m^3 (ref.14) to over 1000 ug/m^3 (ref. 15) have been reported in retort gases. Arsenic concentrations from 5 (ref. 16) to 300 ug/m^3 (ref. 18) have been reported in gas streams from oil shale retorts. No data have been reported on beryllium in oil shale processing gas streams.

Sampling Procedures

The sampling train for both the retort gas and flue gas consisted first of a cold-finger trap (ice bath) followed by an in-line filter holder containing a 0.4 micron filter followed by an impinger containing 150 ml of 5% HNO_3. Next in line was a second impinger containing 150 ml of 5% NaOH solution, followed by two activated charcoal traps in series. A recent publication(19) reported that activated charcoal is an efficient collector for mercury if the flow rate is kept at one liter per minute or less. A schematic of the train is shown in Figure 19. Quality Control/Quality Assurance are discussed in Section VI.

Retort gas and combustor flue gas were sampled during three pilot plant tests; Tests 7, 12 and 19C. Retorting and combustion temperatures were varied for these three tests; average temperatures are given below:

Test Number	Average Retorting Temp, °F	Average Combustion Temp, °F
7	1015	1550
12	930	1430
19C	860	1240

Gas sampling times were approximately one hour with a total of about 30-40 liters of gas collected. Temperature of both gas streams at the point of sampling was ambient, due to cooling of the gases from heat losses. Some of the more volatile metals probably condensed out in various parts of the pilot plant due to this cooling.

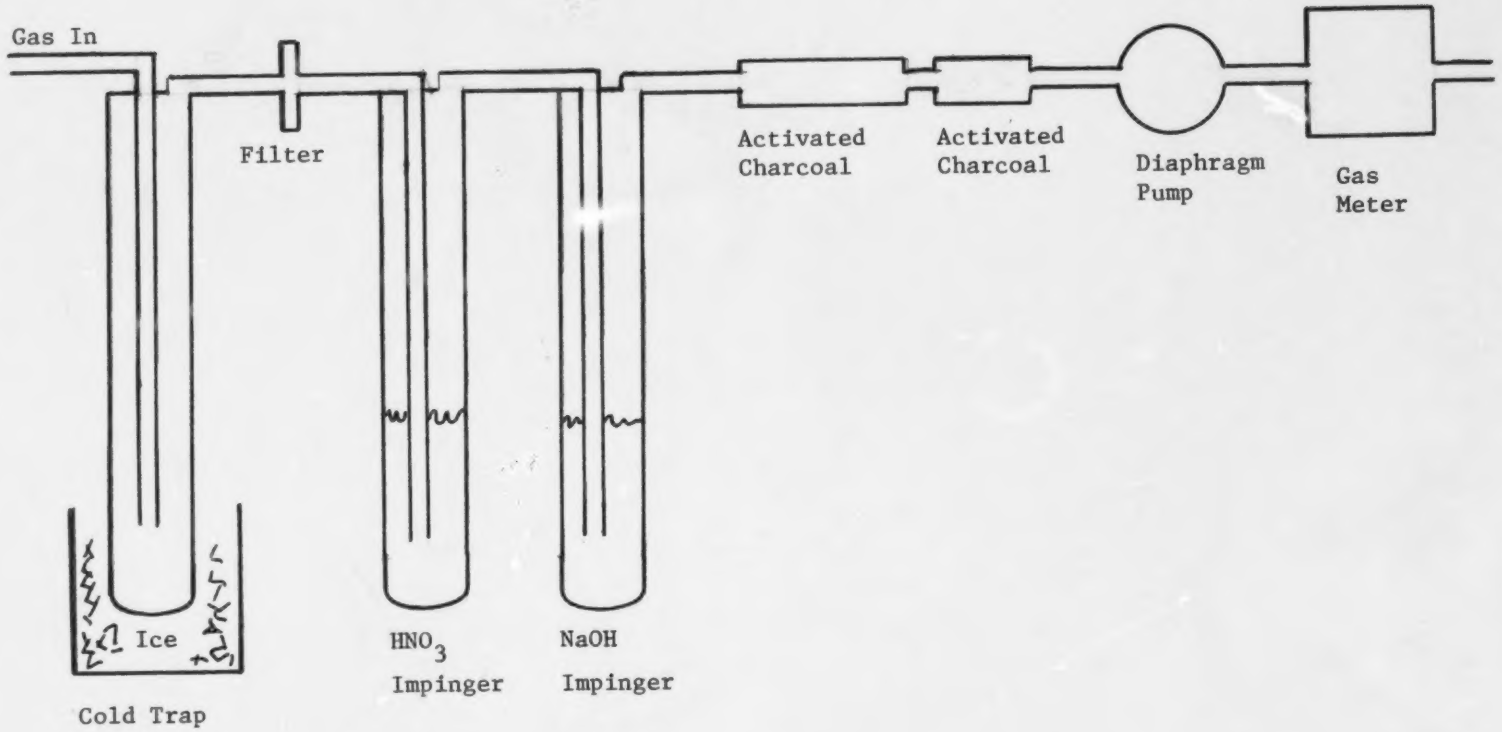
Gas In
Filter
Activated Charcoal
Activated Charcoal
Diaphragm Pump
Gas Meter
Ice
Cold Trap
HNO_3 Impinger
NaOH Impinger

FIGURE 19. SAMPLING TRAIN FOR RECYCLE RETORT GAS AND FLUE GAS.

During Test 12, an aqueous solution containing 3 g/L Hg and 3 g/L Cd (prepared from the nitrate salts) was pumped into the bottom of the combustor to determine their fate in the combustor. The amount of mercury and cadmium fed in the spike represents about 4700 times and 170 times, respectively, the amounts of mercury and cadmium entering the system in the raw shale during the 2 hour spike period.

Corresponding composite samples of raw shale, retort discharge, heat carrier and baghouse ash were taken during the tests.

Analytical Methodology

The aqueous portion of the cold traps, which were very small (the maximum collected during any test was only 1.1 gram) and the HNO_3 and NaOH solutions were digested with HNO_3 according to EPA procedures. Mercury was determined by cold vapor atomic absorption, arsenic by hydride generation AA, cadmium, lead and beryllium by furnace AA and fluoride by specific ion electrode.

The filter samples, which contained very little particulate matter (the largest amount in any run was 0.1 gram) were cut in half. One half was digested with HNO_3 and arsenic, cadmium, lead, beryllium and fluoride determined as described above. The other half of the filter was digested for mercury analysis according to the EPA procedure which uses sulfuric acid, nitric acid, potassium permanganate and potassium persulfate as the digestion media. Mercury was then determined by cold vapor AA.

The activated charcoal samples were digested in HNO_3 and arsenic, cadmium, lead, beryllium and fluoride determined as described above. A separate aliquot of the charcoal was digested with sulfuric acid, nitric acid, potassium permanganate and potassium persulfate; this digest was used for the mercury analysis.

The raw shale, retorted solids, heat carrier and baghouse ash were digested in HNO_3 and arsenic, cadmium, lead and beryllium determined as described above. For the mercury analysis the samples were treated the same as the activated charcoal samples. A lithium metaborate fusion followed by specific ion electrode determination was done for the fluoride analysis.

Discussion of Results

A summary of the analytical results for all the elements analyzed are given in Table 14. Due to the low levels of mercury found in the raw shale (0.025 and 0.015 ppm) and an increase in mass of the retorted solids and heat carrier of between 5 and 6.5 times that of the raw shale, the mercury level in these streams was generally below the detection limit, except for Test 12 in which mercury and cadmium salts were injected into the combustor. It is quite possible that mercury volatilized during retorting or combustion condensed on the cooler parts of the plant equipment. Previous work has reported difficulties in collecting and analyzing mercury in retort gases(8).

TABLE 14. TRACE ELEMENT ANALYSES FROM PILOT PLANT TESTS 7, 12 AND 19C

Test 7 (High Temp.)	Hg	Cd	As	Pb	Be	F
Raw Shale, ppmw	0.025	0.69	56	26	0.66	640
Retorted Solids, ppmw	0.005	0.87	36	24	0.48	240
Heat Carrier, ppmw	0.005	0.86	47	22	0.68	230
Baghouse Ash, ppmw	0.009	0.70	90	20	1.02	700
Retort Gas, ug/m^3	4	184	115,355(a)	2,546(a)	2	35
Flue Gas, ug/m^3	4	26	8	113	9	35
Test 12 (Med. Temp, Metals Spike)						
Retorted Solids, ppmw	0.011	23	37	24	0.64	330
Heat Carrier, ppmw	0.067	24	31	22	0.52	290
Baghouse Ash, ppmw	2.1	51	92	24	1.08	890
Retort Gas, ug/m^3	106	264	88,103(a)	146	2	35
Flue Gas, ug/m^3	24,720	25	9	6	2	35
Test 19C (Low Temp.)						
Raw Shale, ppm	0.015	0.69	54	30	0.68	730
Retorted Solids, ppm	0.005	1.4	42	27	0.64	410
Heat Carrier, ppm	0.005	1.6	35	26	0.56	350
Baghouse Ash, ppm	0.019	9.1	72	25	1.24	780
Retort Gas, ug/m^3	4	2	49	9	2	35
Flue Gas, ug/m^3	22	15	9	9	2	35

ppmw - parts per million by weight.

(a) - Values appear high but are reported as measured. A possible explanation for those high values is that As and Pb from prior runs had condensed within the system and was flushed out by this high temperature run.

A summary of material balances for the elements is given in Table 15. Complete balances are given in later sections. Material balances could only be calculated around the fluid bed combustor because the shale oil and pyrolysis water were not analyzed.

TABLE 15. SUMMARY OF ELEMENTAL BALANCES AROUND COMBUSTOR

	% Recovery					
	Hg	Cd	As	Pb	Be	F
Test 7	(a)	95	139	88	148	119
Test 12	43[b]	65[b]	98	91	89	105
Test 19C	(c)	(c)	87	91	94	90

(a) Mercury values were so low that no balance could be determined.
(b) Includes metal spike.
(c) Not meaningful, due to unknown amount of metals still present from the Hg and Cd spike during Test 12, about forty-eight hours before Test 19C.

Table 16 gives the percentage of trace elements present in the raw shale feed which was found in the retort gas and flue gas. In Test 12 the amount of mercury and cadmium added to the combustor is included as part of the total. Note that although the trace elements were fed to the combustor, significant amounts of mercury (41.3 percent) were found in the retort gas. Mercury and possibly some cadmium were probably deposited on the heat carrier in the combustor and recycled back to the retort where they were re-volatilized.

TABLE 16. PERCENTAGE OF TRACE ELEMENTS PRESENT IN RAW SHALE FOUND IN RETORT GAS AND FLUE GAS

Test 7	% Found In Retort Gas	% Found In Flue Gas
Hg	ND	ND
Cd	2	7
As	13.8	0.03
Pb	0.65	0.8
Be	ND	2.7
F	ND	ND
Test 12		
Hg(a)	0.01	41.3
Cd(a)	0.02	0.005
As	11.2	0.03
Pb	0.03	0.04
Be	ND	ND
F	ND	ND
Test 19C		
Hg(b)	--	--
Cd(b)	--	--
As	0.004	0.03
Pb	0.001	0.7
Be	ND	ND
F	ND	ND

ND = Not detected - below limit of detection which was 4 ug/m^3.

(a) Includes metal spikes.

(b) Not applicable due to unknown amount of Hg and Cd still present from the spiking of these metals in Test 12 spike.

Detailed elemental balances around the combustor for the three tests are given in Tables A-15 to A-20. A mercury balance for Test 7 could not be obtained due to very low concentrations of mercury in the raw shale feed and limitations on the detection limits of the retorted solids which was the feed to the combustor. The only mercury detected was in the baghouse ash which contained 25% of the mercury present in the raw shale. It is reasonable to assume, based on previous investigator's work, that at least 75% or more of the mercury volatilized and deposited on cool surfaces in various parts of the pilot plant. However, it should be remembered that due to the large increase in mass of the retorted solids compared to the raw shale feed, any mercury present in the retorted solids could have been below the detection limits. In Test 12, (metals spike to the combustor) only 43% of the mercury was recovered from the spike addition. Of the 43% recovered, 96% of it was in the combustor flue gas. The high recovery in Test 19C probably reflects the residual amount of mercury still present in the pilot plant from the spike in Test 12.

A good cadmium balance (95%) was obtained in Test 7. In the metals spike, Test 12, only 65% of the cadmium was recovered, the balance probably being deposited on cool surfaces in the pilot plant. The high recovery in Test 19C again reflects the residual metals present from Test 12.

The high arsenic recovery of 139% in Test 7 is probably due to re-volatilization of some arsenic deposited from previous tests. The retorting temperature in this test was 1015°F which is considerably higher than normal and the combustor temperature was 1550°F which was the highest in the test program.

The lead material balances for the three tests are fairly consistent at 90% recovery.

The reasons for the high beryllium recovery of 148% in Test 7 and fluoride recovery of 119% in Test 7 are unknown at this time, but may be similar to that for arsenic.

Listed in Table 17 are the percentages of the total amount of the elements that were found in the various scrubber devices. No elements were found in the filter samples or the second activated charcoal samples.

Where detected, about 75 to 90% of the mercury was found in the first stage charcoal and about 10 to 25% in the nitric acid scrubber.

Essentially all of the cadmium in the flue gas was found in the first stage charcoal except for Test 19C where all of the cadmium was found in the caustic scrubber. In the retort gas, 100% of the cadmium in Test 7 was found in the nitric acid scrubber. In Test 12 about 80% was in the acid scrubber, about 10% in the caustic scrubber and 10% in the charcoal.

In the flue gas of Test 7 and 19C, all of the arsenic was found in the charcoal. In Test 12, about 80% of the arsenic in the flue gas was found in the charcoal and the balance in the cold trap. In the retort gas of Tests 7 and 12, all of the arsenic was found in the cold trap. In Test 19C, about 70% of the arsenic in the retort gas was found in the charcoal and the balance in the caustic scrubber.

In the flue gas of Tests 7 and 19C, all of the lead was found in the caustic scrubber. In the flue gas of Test 12, all of the lead was found in the cold trap.

In Test 7, about 60% of the lead in the retort gas was found in the acid scrubber and the balance in the caustic scrubber. In Test 12, the opposite was true, about 65% of the lead in the retort gas was in the caustic scrubber and the balance was found in the acid scrubber with a small amount in the cold trap. In Test 19C, all of the lead in the retort gas was found in the cold trap.

Only one sample contained beryllium, that being the flue gas of Test 7. All of the beryllium was found on the charcoal.

No fluoride was detected in any of the samples.

No attempt was made to determine the species of the elements present in the gas streams, but it is reasonable to assume that, under the wide variation in operating conditions of the three tests, different species will form and will be collected in different scrubbing media.

Any future sampling of this type should use at least all of the scrubbers that were used in this study.

TABLE 17. PERCENT DISTRIBUTION OF TOTAL ELEMENT CONCENTRATION IN GAS STREAM FOUND IN VARIOUS SCRUBBERS

		Test 7		
Flue Gas	Cold Trap	HNO_3 Scrubber	NaOH Scrubber	First Stage Charcoal
Hg	--	--	--	--
Cd	3.5	--	--	96.5
As	--	--	--	100.0
Pb	0.4	--	99.6	--
Be	--	--	--	100.0
F	--	--	--	--
Retort Gas				
Hg	--	--	--	--
Cd	--	100.0	--	--
As	99.95	--	0.02	0.04
Pb	0.2	61.0	38.8	--
Be	--	--	--	--
F	--	--	--	--
		Test 12		
Flue Gas				
Hg	0.03	22.76	1.09	76.11
Cd	--	--	--	100.0
As	17.4	--	--	82.6
Pb	100.0	--	--	--
Be	--	--	--	--
F	--	--	--	--
Retort Gas				
Hg	6.8	--	17.7	75.5
Cd	0.2	81.7	9.1	9.1
As	99.88	--	0.08	0.04
Pb	1.4	32.9	65.8	--
Be	--	--	--	--
F	--	--	--	--
		Test 19C		
Flue Gas				
Hg	--	11.8	--	88.2
Cd	--	--	100.0	--
As	--	--	--	100.0
Pb	--	--	100.0	--
Be	--	--	--	--
F	--	--	--	--
Retort Gas				
Hg	--	--	--	--
Cd	--	--	--	--
As	--	--	31.7	68.3
Pb	100.0	--	--	--
Be	--	--	--	--
F	--	--	--	--

-- Not Detected.

V. RECOMMENDATIONS ON DESIGN AND OPERATION OF A FLUID BED COMBUSTOR WHICH OPTIMIZES SO_2 AND NO_x CONTROL

Based on the pilot plant data obtained in this study, fluid bed operating conditions are recommended to optimize SO_2 and NO_x control. In general, conditions that favor low SO_2 emissions also favor low CO and trace hydrocarbon emissions but do not favor low NO_x emissions. The general ranges of operating conditions which produced reasonable results both from an operating and emissions viewpoint are given below. Conditions used in the Phase I conceptual design work are shown for comparison in Table 18.

TABLE 18. COMPARISON OF FLUID BED COMBUSTOR OPERATING CONDITIONS

Operating Conditions	Recommended	Conceptual Design
Fluid Bed Temperature, °F	1150 to 1550	1350
Solids Residence Time, min	11 to 14	14
Gas Residence Time, sec.	0.5 to 1.0	1.0
Gas Superficial Velocity, ft/sec	7+	5.0
Flue Gas Oxygen, mole %	2+	3.0
Carbonate Decomposition, %	45+	60
Ca/S Mole Ratio	6+	23
Raw Shale/Spent Shale Ratio	3/97	7/93

This comparison indicates that the conditions chosen for the conceptual design are reasonable and in most cases conservative.

Gas residence time did not affect SO_2, NO_x, CO or trace hydrocarbon emissions over the range evaluated in this program. With this in mind, gas velocities could likely be increased to 10 feet per second or more, which begins to approach the operating range of fast or circulating fluid beds. However, further testing would be needed to determine the upper limits of gas velocity in the bed.

Nitrogen oxide emissions are minimized at the lowest possible oxygen concentration and solids residence time. Oxygen concentrations approaching zero are needed to reduce NO_x levels to less than 100 ppmv.

Mixing raw shale into the spent shale appears to lower NO_x levels to a range of 160-210 ppmv, while SO_2 concentrations range from about 10 to 40 ppmv. Test 19C, where only raw and spent shale were combusted (no retort gas was burned), resulted in the following emissions:

	Test 19C Emissions
CO	0.27 mole%
SO_2	11 ppmv
NO_x	160 ppmv
Trace Hydrocarbons	388 ppmv

This test closely approximates the conceptual design as seen in Table 19 and is an optimum with regard to all emissions.

TABLE 19. COMPARISON OF TEST 19C OPERATING CONDITIONS WITH CONCEPTUAL DESIGN

Operating Conditions	Test 19C	Conceptual Design
Fluid Bed Temperature, °F	1227	1350
Solids Residence Time, min	9.39	14
Gas Residence Time, sec	0.87	1.0
Gas Superficial Velocity, ft/sec	4.41	5.0
Flue Gas Oxygen, mole %	2.6	3.0
Carbonate Decomposition, %	55.3	60
Ca/S Mole Ratio	10.25	23
Raw Shale/Spent Shale Ratio	2.7/97.3	7/93
Organic Carbon Combustion Efficiency, %	88.9*	94

* Since fluid bed temperature did not affect NO_x emissions, the optimum emission and combustion efficiency would likely be obtained at a higher bed temperature that 1227°F.

Since tests with high sulfur input in both retort gas (Test 8) and natural gas (Test 13) produced only 2 ppmv of SO_2 in the flue gas, it is felt that combustion of retort gas and raw shale together would not result in higher SO_2 emissions than shown in Test 19C. That is, it does not appear that sulfur content of the inlet gas has much effect on SO_2 emissions.

VI. QUALITY ASSURANCE/QUALITY CONTROL

A. QA Objectives and Performance

1. Objectives

Table 19A summarizes QA objectives with regard to precision, accuracy and completeness for the key emissions analyses as discussed in the QA/QC plan.

Arsenic determination using hydride generation and mercury determination using cold vapor are difficult for solid samples at low levels and the wide accuracy range reflects the difficulties with these matrices. Beryllium and lead determination methodology will be selected dependent on the levels found early in the testing regimen.

Trace metal scan using X-Ray Fluorescence provides semi-quantititve data. Precision of the counting is excellent, however, interferences limit the accuracy of the individual samples. Comparative values obtained with similar solid products can be very reliable. Standardization methods for individual components can be applied for selected metals. Audit values are expected to be within limits listed.

Hydrogen sulfide and organic sulfur species analyses are most affected by sampling procedures and equipment. Failure to purge sample containers properly, shale dust in sample streams, leaking containers, and gas instability are potential problems which must be recognized. The analyses for organic sulfur compounds are difficult for streams containing large hydrogen sulfide concentrations since this peak can mask the others.

On-stream analyses of gaseous emissions (oxygen, sulfur dioxide, nitrogen oxides and carbon monoxides) are most affected by potential problems with the sample line, e.g., plugging with solids and condensates. Filters, condensers and traps have been installed to minimize such problems.

2. Performance

QA performance with regard to sampling and analytical methodology are discussed in the following sections B through D for each sample and/or analysis employed.

QA performance in the key emissions data areas was generally very good and met the defined objectives. Results on mercury emissions were outside the range of objectives probably due to the very low levels of mercury encountered (in many cases mercury was below detection limits).

TABLE 19A. SUMMARY OF PRECISION ACCURACY AND COMPLETENESS OBJECTIVES

Measurement Parameter (Method)	Reference	Experimental Conditions	Precision Standard Deviation	Accuracy	Completeness
Total Sulfur for Solids (X-Ray Fluorescence)	ASTM D2622-82 Adjusted for matrix difference	Laboratory standards prepared with analytical reagents: Synthetic matrix backgrounds, NBS oil reference standards	±10%	±10%	80%
Fluorine (Ion selective electrode)	EPA 600/4-79-020 March 1983, Method 340.2	EPA Reference Standards	±15%	±10%	70%
Arsenic (Hydride atomic absorption)	EPA 600/4-79-020 March 1983, Method 206.3	EPA Reference Standards	±20%	±20%	70%
Beryllium, Lead (Atomic Absorption Direct)	EPA 600/4-79-020 March 1983, Method 210.1 239.1	EPA Reference Standards	±10%	±5%	80%
Beryllium, Lead (Atomic Absorption Furnace)	EPA 600/4-790-020 March 1983, Methods 210.2, 239.2	EPA Reference Standards	±15%	±15%	70%
Trace Metals Scan (X-Ray Fluorescence)	Instrument manufacturer guidelines	Standard Laboratory Preparations in cellulose, wavelength calibration with Conostan oil, tube background calibration checks	±10%	±25%	80%
Cadmium (Atomic Absorption Direct)	EPA 600/4-79-020 March 1983, Method 213.1	EPA Reference Standards	±10%	±10%	80%
Mercury (Atomic Absorption Cold Vapor)	EPA 600/4-79-020 March 1983 Method 245.1	EPA Reference Standards	±20%	±20%	70%
Hydrogen Sulfide, Organic Sulfur Species	Supelco Bulletin #722	Gas Chromatography with Flame Photometric Detection NBS Certified Permeation Tubes Used for Calibrations	±20%	±20%	70%
Oxygen Sulfur Dioxide Nitrogen Oxides Carbon Monoxide	Paramagnetic O_2 Analyzer Pulsed Fluorescence Analyzer Chemiluminescent N_2 Analyzer Infra-red Analyzer	On-Line Analyzers Calibrated With NBS Traceable Gas	±15%	±15%	80%

B. Sampling Methodology and Results

Six solid/gas streams were routinely sampled as follows. Each stream is identified diagramatically in Figure 7.

Stream	Description
1	Raw Shale Feed
2	Retorted Solids
3	Heat Carrier
4	Baghouse Ash
5	Retort Gas to Combustor
6	Flue Gas

A list of sample analyses and frequency of analysis for each stream is given in Table 20.

1. Sampling Methodology

a. Raw Shale Feed Samples (Stream 1)

Raw shale samples were taken at the inlet to the steam heated screw conveyor feeding the retort. These relatively cool samples (50°F to 160°F) were taken as follows:

1. Open sample point valve and drain a quantity of solids to assure a clean flow path. Discard these solids.
2. Keeping valve open, drain solids into a one quart sample can.
3. Close sample point valve. Seal sample can with lid and label can.

TABLE 20. SAMPLE ANALYSES AND FREQUENCY OF ANALYSIS

Analysis	Raw Shale	Retorted Solids	Heat Carrier	Baghouse Ash	Retort Gas	Flue Gas
Fischer Assay	S					
Moisture	S					
Total Carbon	S	R	R	R		
Mineral Carbon	S	R	R	R		
Hydrogen	S	R	R	R		
Nitrogen	S	R	R	R		
Sulfur	S	R	R	R		
Mineral Breakdown	S	NR	NR	NR		
Particle Size	S	NR	NR	NR		
GC Scan					R	R
Trace Hydrocarbon						R
Continuous Sulfur Analyzer					R	
O_2, NO_x, CO, SO_2 Continuous Analyzers						R
Ammonia						NR
Ca, Mg	S	NR	NR	NR		

S = Spot analysis done for two tests
NR = Non-routine analysis done for 3 to 8 tests
R = Routine analysis done for 20 tests

b. Retorted Solids and Heat Carrier Samples (Streams 2 and 3)

These relatively hot solids (about 900°F for the retorted solids and 1100 to 1550°F for the heat carrier) required special sampling procedures. Each solids sample point was provided with a ball or plug valve which when opened allows solids to drain by gravity into the solids sampler. The solids sampler consisted of a one foot length of two inch diameter pipe closed at the bottom and fitted with a ball valve at the top end. Purge connections were provided on the sampler pipe at both top and bottom. To take a solids sample these steps were followed:

1. Purge sampler with nitrogen.
2. Open sample point valve and drain a quantity of solids to assure a clear flow path. Discard these solids.
3. Connect sampler, open sampler valve and sample point valve and allow solids to drain into sampler.
4. Close sampler and sample point valves and disconnect sampler.
5. Quench sampler in water.
6. Open sampler valve and dump contents of sampler into sample can, seal can with lid and label can.

c. Baghouse Ash Samples (Stream 4)

These samples were taken at the flue gas inlet to the baghouse. A three inch sample line with a ball valve was teed into the flue gas line. Warm flue gas (about 300°F to 400°F) containing combusted fines was sampled as follows:

1. The sample valve was opened and dusty gas vented for about 10 seconds to clean the line.
2. The valve was closed and the open end of a 6-inch diameter baghouse bag was tied to the end of the sample line.
3. The valve was opened and dusty flue gas was vented through the bag for about 5-10 minutes, or until about one quart of solids was collected.
4. The valve was closed and the solids collected in the bag were put into a quart sample can. The can was sealed with a lid and labeled.

d. Retort Gas and Flue Gas Samples (Streams 5 and 6)

These gas samples were taken in glass flow-through bombs having glass stopcocks on either end. Samples were taken through sampling valves on 1/4-inch tubing. Samples were taken as follows:

1. The sample valve was opened and gas was allowed to flow for a few seconds to assure adequate gas flow and pressure.
2. The valve was closed and the sample bomb was attached to the sample tubing with tight fitting clear plastic tubing.
3. The stopcocks were both opened and then the sample valve and flow was verified by allowing the gas to bubble through a clear plastic water bottle. If no flow was observed, the stopcocks were cleaned with a small wire.
4. After good gas flow was established, the gas was allowed to flow through the bomb for a minimum of five minutes and a maximum of ten minutes.

5. To maximize gas pressure in the bomb and prevent air contamination, the downstream stopcock was closed first, followed by the upstream stopcock and finally the sample valve.
6. The sample bomb was removed from the plastic tubing and labeled.

2. Sampling Results

No problems were encountered sampling the raw shale, retorted solids, heat carrier and baghouse ash samples.

The status of the retort gas sampling for the 44 tests can be summarized as follows:

Retort Gas Sampling

	Number of Tests
Sulfur Analysis Only	1
Complete GC Analysis	22
No Sample Taken	12
Bad Samples	2
No Retort Gas to Combustor	7
TOTAL	44

Of 25 retort gas samples taken, only two were improperly taken so that no analysis was possible.

Retort gas samples were taken near the point where the retort gas entered the combustor. On five tests, the pulsating pressure in the fluid bed caused large pressure spikes which forced solids from the bed into the retort gas line. When retort gas samples were taken some shale dust entered the glass sample bombs and absorbed all of the H_2S and part or all of the CO_2. On one test, so much dust entered the bomb that no analysis was possible.

The status of flue gas sampling during the 44 tests is as follows:

Flue Gas Samples

	Number of Tests
Complete GC Analysis	28
No Sample Taken	11
Bad Samples (air in sample)	5
TOTAL	44

C. Analytical Methodology and Results

1. Laboratory Analyses

Mineral Carbon (Coulometric Analysis)

Essentially all of the solid samples analyzed for mineral carbon were done in duplicate. A blank and reference sodium carbonate sample were analyzed before and after every seven to ten samples. Representative duplicate values are given in Table 21.

TABLE 21. SUMMARY OF DUPLICATE MINERAL CARBON ANALYSES

Sample No.	Sample Description	Duplicates, wt%
54173	Baghouse Ash	2.24, 2.20
54174	Raw Shale	4.42, 4.48
54175	Heat Carrier	0.34, 0.32
54176	Retorted Solids	0.50, 0.66
54183	Retorted Solids	0.85, 0.79
54184	Heat Carrier	0.34, 0.32
54185	Baghouse Ash	0.98, 0.96

Total Carbon, Hydrogen and Nitrogen (Elemental Analyzer)

All of the solid samples analyzed for total carbon, hydrogen and nitrogen were done in duplicate. A blank is run once per batch of samples and a reference shale sample is run before and after each four samples. Representative results are given in Table 22.

TABLE 22. SUMMARY OF DUPLICATE TOTAL CARBON, HYDROGEN AND NITROGEN ANALYSES

		Duplicates, wt%		
Sample No.	Sample Description	Total C	Total H	Total N
54173	Baghouse Ash	2.33, 2.16	0.03, 0.01	0.10, 0.14
54174	Raw Shale	22.20, 21.99	2.30, 2.34	0.64, 0.63
54175	Heat Carrier	0.52, 0.58	0.03, 0.03	0.03, 0.03
54176	Retorted Solids	1.27, 1.07	0.03, 0.01	0.05, 0.05
54183	Retorted Solids	1.39, 1.33	0.02, 0.01	0.05, 0.06
54184	Heat Carrier	0.26, 0.15	0.01, 0.01	0.01, 0.01
54185	Baghouse Ash	0.85, 0.90	0.01, 0.01	0.08, 0.10

Sulfur (X-ray Fluorescence)

All of the solid samples analyzed for total sulfur were done in duplicate. Calibration standards for the x-ray analyses were prepared from synthetically produced shale media and varying amounts of $CaSO_4$. Representative results are given in Table 23.

TABLE 23. SUMMARY OF DUPLICATE SULFUR ANALYSES

Sample No.	Sample Description	Duplicates, wt%
54130	Heat Carrier	0.44, 0.44
54136	Heat Carrier	0.55, 0.55
54157	Retorted Solids	0.78, 0.79
54128	Baghouse Ash	0.99, 0.99
54185	Baghouse Ash	1.71, 1.72
54135	Retorted Solids	0.66, 0.66

With each batch of samples, usually between 5 and 10, a spike was made to the sample and percent recovery determined. Representative results are given in Table 24.

TABLE 24. SUMMARY OF SPIKE RECOVERIES

Sample No.	Sample Description	Duplicates, wt%
54130	Heat Carrier	104.2, 99.2
54157	Retorted Solids	108.4, 108.0
54128	Baghouse Ash	95.4, 94.6
54185	Baghouse Ash	94.1, 94.5
54135	Retorted Solids	105.0, 106.7

Mole Percent Concentrations of Gases by Gas Chromatography

Linear calibration factors and ranges of concentrations are determined for specific gas components found in retort gas and flue gas. Calibration factors were determined by injecting known concentrations of the following components:

Hydrogen
Oxygen
Nitrogen
Carbon Monoxide
Carbon Dioxide
Hydrogen Sulfide
Methane
Ethane
Ethene
Propane
Propene

isoButane
normal Butane
isoButylene + Butene-1
trans-Butene-2
cis-Butene-2
iso-Pentanes
normal Pentane
Pentenes
normal Hexane
normal Heptane

The method of analysis was gas chromatography using thermal conductivity as the detection system. The quantitation method was external standard calibration using certified calibration gases. Daily calibration checks are made by analyzing standard gases as samples.

Total Trace Hydrocarbons by Gas Chromatography

Total trace hydrocarbons in the flue gas were determined by gas chromatography with flame ionization as the detection method. A calibration curve giving response factors and showing linearity was established at the beginning of the test period by analyzing known concentrations of hydrocarbon mixtures in the part per million range. Hydrocarbon mixtures were certified and traceable to EPA standards. A daily calibration check point was determined by analyzing an EPA calibration standard mixture and chromatographic conditions adjusted to keep the check point on the initial calibration curve.

Sample and calibration gases were injected using gas tight syringes and quantitated using the external standard calibration method. Standard hydrocarbon mixtures were analyzed and calculated as total butane. All samples were reported on a normal butane equivalent.

Determination of Carbonyl Sulfide, Hydrogen Sulfide, Carbon Disulfide, Sulfur Dioxide, Methyl Mercaptan and Ethyl Mercaptan by Gas Chromatography Using Flame Photometric Detection

Trace sulfur component analysis in the part per million range was determined using gas chromatography and flame photometric detection. Calibration curves and response factors were established for each component at the beginning of the testing period. Calibration gases in the part per million range were prepared using permeation tubes and diffusion wafers certified and traceable to NBS materials. A daily calibration check of EPA certified sulfur dioxide gas at 50 ppm was used to insure detector response stability throughout the testing period.

Calibration gases and samples were injected using gas tight syringes. Sulfur species were detected using a flame photometric detector with a sulfur specific optical filter of 394 nanometers.

Particle Size

Particle size analysis by screening using 4, 8, 12, 20, 40 and 80 mesh screens were done on selected solids samples. One quart samples were run through a splitter until about 500g were obtained. The 500g was screened and the retains on each screen were weighed and particle size distribution calculated. The -80 mesh material was further analyzed on an automatic particle size analyzer in triplicate. Results for a sample of baghouse ash are given below:

-80 Mesh in Microns, wt%	Sample No. 54173
-176 + 125	0, 0, 0
-125 + 88	0, 0, 0
-88 + 62	0, 0, 0
-62 + 44	0, 0, 0
-44 + 31	0, 0, 0
-31 + 22	10.7, 9.9, 9.4
-22 + 16	10.3, 8.1, 8.6
-16 + 11	13.9, 13.2, 12.2
-11 + 7.8	21.4, 22.0, 22.1
-7.8 + 5.5	16.3, 16.9, 17.6
-5.5 + 3.9	11.9, 13.1, 13.1
-3.9 + 2.8	7.4, 8.1, 8.2
-2.8 + 1.9	7.7, 8.4, 8.6

2. Continuous Analyzers

A continuous total sulfur analyzer was used on the retort gas. This analyzer did not perform consistently, and although it was calibrated once or more each day, it tended to drift out of calibration quickly. Data from this analyzer was considered unreliable and was not used in any of the correlations.

Continuous oxygen, carbon monoxide, sulfur dioxide and nitrogen oxides analyzers were used on the flue gas. These analyzers performed well and had essentially no downtime. These analyzers were calibrated every day or every other day using zero and span gases traceable to NBS standards. The flue gas was conditioned by a filter, chiller and silica gel dryer before injection into the analyzers. A comparison of analyzer oxygen concentration with gas chromatography oxygen content is shown in Figure 20.

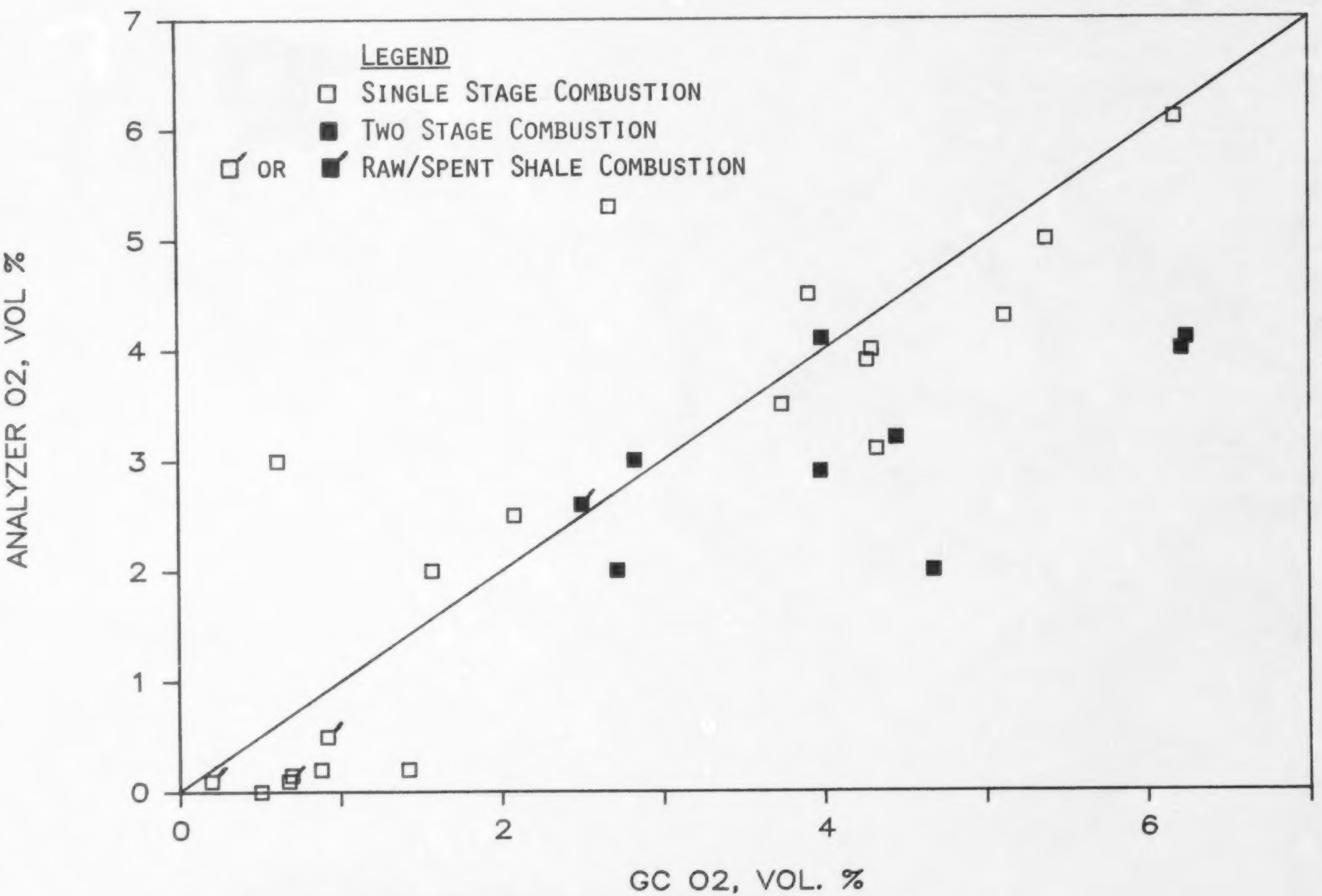

FIGURE 20. COMPARISON OF FLUE GAS OXYGEN ANALYSES.

D. Trace Element Methodology and Results

Sampling and analyses for the trace elements mercury, cadmium, arsenic, lead, beryllium and fluoride are given in a previous section.

For the atomic absorption analyses of mercury (cold vapor), arsenic (hydride generation), cadmium, lead and beryllium (furnace), reagent blanks and calibration standards were run before and after every fifth sample. Various types of samples were spiked with known amounts of analyte and the percentage recovery determined. Results are given in Table 25.

TABLE 25. SUMMARY OF SPIKE RECOVERIES

Mercury

Sample No.	Sample Description	% Recovery of Spike
626-49-5	Charcoal	95
626-53-3	Acid Scrubber	95
626-53-4	Caustic Scrubber	117
626-53-5	Charcoal	103
54173	Baghouse Ash	92

Cadmium

Sample No.	Sample Description	% Recovery of Spike
626-46-4	Caustic Scrubber	120
662-47-3	Acid Scrubber	77
54174	Raw Shale	82

Arsenic

Sample No.	Sample Description	% Recovery of Spike
54174	Raw Shale	110
54554	Retorted Solids	98

Lead

Sample No.	Sample Description	% Recovery of Spike
626-47-3	Acid Scrubber	84
626-54-4	Acid Scrubber	76
54553	Raw Shale	79

Beryllium

Sample No.	Sample Description	% Recovery of Spike
54553	Raw Shale	88
626-47-3	Acid Scrubber	112

Fluoride

Sample No.	Sample Description	% Recovery of Spike
54174	Raw Shale	76

Duplicate analyses were also run on various samples. Results are given in Table 26.

TABLE 26. SUMMARY OF DUPLICATE ANALYSES

Mercury

Sample No.	Sample Description	Duplicates
626-50-4	Caustic Scrubber Digest	76, 80 ng/25ml
662-54-6	Charcoal	173, 152 ng/g
54556	Baghouse Ash	20, 18 ng/g

Cadmium

Sample No.	Sample Description	Duplicates
626-49-3	Acid Scrubber Digest	≦0.001, 0.001 ug/ml
626-49-4	Caustic Scrubber Digest	0.001, 0.001 ug/ml
626-53-3	Acid Scrubber Digest	0.001, 0.001 ug/ml
626-54-4	Caustic Scrubber Digest	0.001, 0.001 ug/ml
626-49-5	Charcoal	0.010, 0.007 ug/ml
626-53-5	Charcoal	0.004, 0.002 ug/ml

Arsenic

Sample No.	Sample Description	Duplicates
626-49-3	Acid Scrubber Digest	<5, <5 ng/5ml
626-49-4	Caustic Scrubber Digest	<5, <5 ng/5ml
626-53-3	Acid Scrubber Digest	<5, <5 ng/5ml
626-53-4	Caustic Scrubber Digest	5.8, 5.0 ng/5ml
626-49-5	Charcoal Digest	0, 7 ng/5ml
626-53-5	Charcoal Digest	42, 32 ng/5ml

Lead

Sample No.	Sample Description	Duplicates
626-49-3	Acid Scrubber Digest	0.002, 0.001 ug/ml
626-49-4	Caustic Scrubber Digest	0.001, 0.001 ug/ml
626-53-3	Acid Scrubber Digest	<0.001, 0.001 ug/ml
626-49-5	Charcoal Digest	<0.001, <0.001 ug/ml

Beryllium

Sample No.	Sample Description	Duplicates
626-49-3	Acid Scrubber Digest	<0.001, <0.001 ug/ml
626-49-4	Caustic Scrubber Digest	<0.001, <0.001 ug/ml
626-53-3	Acid Scrubber Digest	<0.001, <0.001 ug/ml
626-53-4	Caustic Scrubber Digest	<0.001, <0.001 ug/ml
626-49-5	Charcoal Digest	<0.001, <0.001 ug/ml
626-53-5	Charcoal Digest	<0.001, <0.001 ug/ml

Fluoride

Sample No.	Sample Description	Duplicates
54554	Retorted Solids	409, 386 ug/g

VII. REFERENCES

1. Denver Research Institute, "Pollution Control Technical Manual: Modified In-situ Oil Shale Retorting Combined with Lurgi Surface Retorting," U.S. Environmental Protection Agency, EPA-600/8-83-004 (NTIS PB83-200-121), 1983. Cited on pp. 1, 17.

2. Denver Research Institute, "Pollution Control Technical Manual: Tosco II Oil Shale Retorting with Underground Mining," U.S. Environmental Protection Agency, EPA-600/8-83-003 (NTIS PB83-200-212), 1983. Cited on page 1.

3. McCarthy, H.E., "Fluidized Bed Combustion of Oil Shale", Sixteenth Oil Shale Symposium Proceedings, Colorado School of Mines, April 13-15, 1983, Golden, Colorado, pp. 469-476. Cited on page 3.

4. Hall, R. N., "Hydrocarbon Solids Process - HSP Technology", AIChE Spring National Meeting, Anaheim, California, June 8, 1982. Cited on page 6.

5. Denver Research Institute, Private correspondence with Kishor Gala. Cited on page 17.

6. Denver Research Institute, Pollution Control Technical Manual: Lurgi Oil Shale Retorting With Open Pit Mining," U.S. Environmental Protection Agency, EPA-600/8-83-005 (NTIS PB83-200-204), 1983. Cited on page 17.

7. Fox, J. P., "Distribution of Mercury during Simulated In-situ Oil Shale Retorting", Environmental Science and Technology, 19, pp 316-322, April, 1985. Cited on page 48.

8. Hodgson, A. T., et. al., "Mercury Mass Distribution During Laboratory and Simulated In-situ Oil Shale Retorting", Lawrence Berkeley Laboratory, Berkeley, CA, February, 1982, Report LBL-12908. Cited on pp. 48, 50.

9. Hodgson, A. T., Pollar, M. J., Brown, N. J., "Mercury Emissions from a Modified In-situ Oil Shale Retort", Atmos. Environ. 18, pp. 247-253, 1984. Cited on page 48.

10. Olsen, K. B., "Characterization of Mercury, Arsenic and Selenium in the Product Streams of the Pacific Northwest Laboratory 6-Kg, Retort", Richland, Washington, Prepared for the U.S. DOE, Contract DE-AC06-76RL01830, July, 1985. Cited on page 48.

VII. REFERENCES (continued)

11. Fruchter, J. S., et. al., "Elemental Partitioning in Aboveground Oil Shale Retort Pilot Plant", Environmental Science and Technology, November, 1980. Cited on page 48.

12. Fox, J. P., et. al., "The Partitioning of As, Cd, Cu, Hg, Pb and Zn During Simulated In-situ Oil Shale Retorting", 10th Annual Oil Shale Symposium, Golden, Colorado, 1977. Cited on page 48.

13. Fox, J. P., et. al., "Partitioning of Major, Minor and Trace Elements During Simulated In-situ Oil Shale Retorting in a Controlled State Retort", 12th Annual Oil Shale Symposium, Golden, Colorado, 1979. Cited on page 48.

14. Rinaldi, G. M., Delaney, J. L., and Hedley, W. H., "Environmental Characterization of Geokinetics' In-Situ Oil Shale Retorting Technology", Two Volumes, U.S. EPA Report EPA 600/7-81-021a (1981) Main Report and EPA 600/7-81-021b (1981) Appendices, NTIS PB 81 163727 and PB 81 163735,respectively. Cited on page 48.

15. Hodgson, A. T., unpublished data on Cd in gases from a Fischer-Assay-type oil shale retort, Lawrence Berkeley Laboratory, Berkeley, CA (1985). Cited on page 48.

16. Ondov, J. M. and others, "Measurements of Potential Atmospheric Pollutants in Off-Gases from the Lawrence Livermore National National Laboratory's 6-Tonne Retort, Experiment L-3", Lawrence Livermore National Laboratory Report UCRL-53265 (1982). Cited on page 48.

17. Fruchter, J. S., Wilkerson, C. L., Evans, J. C., Sanders R. W., and Abel, K. W., "Source Characterization Studies at the Paraho Semiworks Oil Shale Retort", Battelle Pacific Northwest Laboratory Report PNL-2945 (1981). Cited on page 48.

18. UNOCAL, "Environmental Monitoring Plan Outline, Parachute Creek Shale Oil Program Phase I Advanced Technology Program", Report Submitted to Synthetic Fuels Corporation (1985). Cited on page 48.

19. Dummarey, R., Dams, R., Hoste, J., "Comparison of the Collection and Desorption Efficiency of Activated Charcoal, Silver and Gold for the Determination of Vapor-Phase Atmospheric Mercury", Anal. Chem., 1985, pp. 2638-2643. Cited on page 48.

APPENDIX A

DATA FROM FLUIDIZED BED TESTS

TABLE A-1. SUMMARY OF FLUID BED COMBUSTOR TESTS

Test Number Test Date Test Time	1 10-15-85 1740	1A 10-16-85 1230	2 10-16-85 1730	3 10-17-85 0448	4 10-16-85 2345	5 10-17-85 0730	6 10-17-85 1120	6A 10-17-85 1225	6B 10-17-85 1410	6C 10-17-85 1900	6D 10-17-85 1930	6E 10-17-85 2015	6R 10-17-85 2030	7 10-18-85 1330	7A 10-18-85 1420	7AA 10-18-85 1530	7B 10-18-85 1630
Fluid Bed Temperature, °F	1344	1359	1367	1269	1250	1145	1179	1167	1174	1147	1147	1179	1179	1558	1487	1553	1552
Retort Gas to Combustor, SCFM	3.79	4.86	4.55	3.41	4.12	3.44	3.29	3.23	3.27	3.23	3.16	3.16	2.89	5.90	5.74	6.25	6.66
H_2S in Retort Gas, mole %	0.50	0.63	1.80	0.47	1.44	0.43	0.87	(a)	(a)	(i)	(i)	(i)	3.21	5.34	(a)	(a)	1.51
Raw Shale to Combustor, lb/hr	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Number of Combustion Stages	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Overfire Air, Point of Injection	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Solid and Gas Samples Taken	X	X	X	X	X	X	X		Flue Gas Sample				X	X	Flue Gas Sample		Gas Samples
Analysis of Solid Samples	(No flue gas sample)																
Raw Shale Analysis[e]														X			
Partial Solids Analysis[f]			X		X		X										
Complete Solids Analysis[g]														X			
Trace Metals Analysis[h]														X			
Baghouse Ash Samples Taken For Leaching Evaluation																	
Comments	Retort gas w/o H_2S spike	Retort gas w/o H_2S spike	Retort gas with H_2S spike	Retort gas with H_2S spike	Retort gas with H_2S spike	Retort gas with H_2S spike	Retort gas with H_2S spike	Retort gas with H_2S spike	Retort gas with H_2S spike	Retort gas with H_2S spike	Retort gas with H_2S spike	Retort gas with H_2S spike	Retort gas with H_2S spike	Retort gas with H_2S spike	Retort gas with H_2S spike	Retort gas with H_2S spike	Retort gas with H_2S spike

(a) No retort gas sample taken.
(b) Bad retort gas sample.
(c) Shale dust in retort gas sample absorbed H_2S.
(d) Natural gas and H_2S fed to combustor.
(e) Raw shale analysis included moisture, Fischer Assay, total and mineral carbon, hydrogen, nitrogen, sulfur, calcium and magnesium, particle size.
(f) Partial solids analysis included total and mineral carbon, hydrogen, nitrogen, and sulfur on retorted solids, combusted solids (heat carrier) and combusted fines (baghouse ash) for 12 tests.
(g) Complete solids analysis included total and mineral carbon, hydrogen, nitrogen, sulfur, calcium, magnesium, and particle size on retorted solids, combusted solids (heat carrier) and combusted fines (baghouse ash) for 8 tests.
(h) Trace metals analysis for arsenic, cadmium, mercury, beryllium, lead and fluorine in raw shale, retorted solids, combusted solids (heat carrier), combusted fines (baghouse ash), retort gas and combustor flue gas.

(continued)

TABLE A-1. (continued)

Test Number Test Date Test Time	7C 10-18-85 1900	7D 10-18-85 2045	8 10-18-85 1835	9 10-22-85 0505	10P 10-22-85 1135	10 10-22-85 1250	11 10-23-85 1130	11A 10-22-85 2205	11B 10-22-85 2245	11C 10-23-85 0030	11D 10-23-85 0225	12 10-23-85 1745	12A 10-23-85 1900	13 10-23-85 2000	14 10-24-85 1030	15 10-24-85 0425	16 10-24-85 1415
Fluid Bed Temperature, °F	1508	1415	1441	1363	1339	1363	1494	1428	1366	1384	1354	1424	1429	1447	1134	1170	1127
Retort Gas to Combustor, SCFM	5.62	4.93	4.60	4.09	3.89	3.87	6.03	4.45	4.53	4.14	3.43	5.79	6.23	4.40	5.50	6.36	4.73
H_2S in Retort Gas, mole %	(b)	3.77	9.28	0.81	(a)	3.94	1.18	(c)	(c)	3.90	4.11	(c)	(a)	(d)	3.85	1.98	(a)
Raw Shale to Combustor, lb/hr	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Number of Combustion Stages	1	1	1	1	1	2	2	1	2	2	2	2	2	2	1	2	1
Overfire Air, Point of Injection	--	--	--	--	--	4.5'above dist.	4.5'above dist.	--	4.5'above dist.	4.5'above dist.	4.5'above dist.	4.5'above dist.	4.5'above dist.	4.5'above dist.	--	4.5'above dist	--
Solid and Gas Samples Taken	GasSamples	GasSamples	X	X	Flue Gas Sample	X	X	X	X	X	X	X		X	X	X	
Analysis of Solid Samples																	
Raw Shale Analysis[e]																	
Partial Solids Analysis[f]						X		X	X	X	X						
Complete Solids Analysis[g]			X				X					X		X	X		
Trace Metals Analysis[h]												X					
Baghouse Ash Samples Taken For Leaching Evaluation							X								X		
Comments	Retort gas with H_2S spike	Retort gas with H_2S spike	Retort gas with H_2S spike	Retort gas with H_2S spike	Retort gas with H_2Sspike	Retort gas with H_2S spike	Retort gas with H_2S spike	Retort gas with H_2S spike	Retort gas with H_2S spike	Retort gas with H_2S spike	Retort gas with H_2S spike	Retort gas with H_2S spike	Natural gas with H_2S spike	Retort gas with H_2S spike	Retort gas with H_2S spike	Retort gas with H_2S spike	Retort gas with H_2S spike

(a) No retort gas sample taken.
(b) Bad retort gas sample.
(c) Shale dust in retort gas sample absorbed H_2S.
(d) Natural gas and H_2S fed to combustor.
(e) Raw shale analysis included moisture, Fischer Assay, total and mineral carbon, hydrogen, nitrogen, sulfur, calcium and magnesium, particle size.
(f) Partial solids analysis included total and mineral carbon, hydrogen, nitrogen, and sulfur on retorted solids, combusted solids (heat carrier) and combusted fines (baghouse ash) for 12 tests.
(g) Complete solids analysis included total and mineral carbon, hydrogen, nitrogen, sulfur, calcium, magnesium, and particle size on retorted solids, combusted solids (heat carrier) and combusted fines (baghouse ash) for 8 tests.
(h) Trace metals analysis for arsenic, cadmium, mercury, beryllium, lead and fluorine in raw shale, retorted solids, combusted solids (heat carrier), combusted fines (baghouse ash), retort gas and combustor flue gas.

(continued)

TABLE A-1. (continued)

Test Number Test Date Test Time	17A 10-24-85 2000	17B 10-24-85 2130	17C 10-25-85 0030	17D 10-25-85 0130	18 10-25-85 0550	19A 10-25-85 1230	19B 10-25-85 1330	19C 10-25-85 1430	20P 10-25-85 1610	20 10-25-85 1700
Fluid Bed Temperature, °F	1299	1376	1403	1370	1367	1245	1200	1227	1295	1268
Retort Gas to Combustor, SCFM	0	0	0	0	4.87	0	0	0	5.11	5.10
H_2S in Retort Gas, mole %	--	--	--	--	(c)	--	--	--	(a)	(b)
Raw Shale to Combustor, lb/hr	133.1	133.1	133.1	133.1	0	94.7	94.7	94.7	0	0
Number of Combustion Stages	1	1	1	2	1	2	2	2	1	2
Overfire Air, Point of Injection	--	--	--	16.5'above dist.	--	6.5'above dist.	6.5'above dist.	6.5'above dist.	--	6.5'above dist.
Solid and Gas Samples Taken	X	X	X		X			X		X
Analysis of Solid Samples										
Raw Shale Analysis(e)								X		
Partial Solids Analysis(f)	X		X		X					X
Complete Solids Analysis(g)		X						X		
Trace Metals Analysis(h)								X		
Baghouse Ash Samples Taken For Leaching Evaluation		X								
Comments	Raw shale to combustor, no retort gas or H_2S	Raw shale to combustor, no retort gas or H_2S	Raw shale to combustor, no retort gas or H_2S	Raw shale to combustor, no retort gas or HS	Retort gas with H_2S spike	Raw shale to combustor, no retort gas or H_2S	Raw shale to combustor, no retort gas or H_2S	Raw shale to combustor, no retort gas or H_2S	Retort gas w/o H_2S spike	Retort gas w/o H_2S spike

---

(1) No retort gas sample taken.

(2) Bad retort gas sample.

(3) Shale dust in retort gas sample absorbed H_2S.

(4) Natural gas and H_2S fed to combustor.

(5) Raw shale analysis included moisture, Fischer Assay, total and mineral carbon, hydrogen, nitrogen, sulfur, calcium and magnesium, particle size.

(6) Partial solids analysis included total and mineral carbon, hydrogen, nitrogen, and sulfur on retorted solids, combusted solids (heat carrier) and combusted fines (baghouse ash) for 12 tests.

(7) Complete solids analysis included total and mineral carbon, hydrogen, nitrogen, sulfur, calcium, magnesium, and particle size on retorted solids, combusted solids (heat carrier) and combusted fines (baghouse ash) for 8 tests.

(8) Trace metals analysis for arsenic, cadmium, mercury, beryllium, lead and fluorine in raw shale retorted solids, combusted solids (heat carrier), combusted fines (baghouse ash), retort gas and combustor flue gas.

TABLE A-2. FLUID BED COMBUSTOR OPERATING CONDITIONS

	Single Stage Combustion																
Test Number	1	1A	2	3	4	5	6	6A	6B	6C	6D	6E	6R	7	7A	7AA	7B
Temperature, °F																	
Inlet Gas Heater	1396	1385	1151	1011	782	1123	1092	1100	1136	1389	1330	1269	1269	1428	1427	1432	1395
Fluid Bed	1344	1359	1367	1269	1250	1145	1179	1167	1174	1147	1147	1179	1179	1558	1487	1553	1552
Freeboard	1446	1431	1447	1451	1444	1477	1452	1439	1461	1412	1435	1460	1460	1551	1563	1576	1589
Baghouse	400	378	379	395	361	414	355	384	367	368	379	358	358	324	372	382	329
Stack	275	260	275	273	223	268	240	240	250	250	250	250	250	245	245	245	240
Pressure, Inches Water																	
Fluid Bed (6 in. above distributor)	79	81	81	91	71	95	79	91	83	77	69	70	70	85	92	88	71
Freeboard	34	33	35	40	30	46	26	37	32	33	28	26.5	26.5	40	44	44	30
Flow Rates to Combustor																	
Retorted Solids, lb/hr	2487	2662	2601	3404	3352	3395	3343	3345	3343	3158	3062	3014	3014	2598	2620	2620	2620
Raw Shale, lb/hr	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Retort Gas, SCFM	3.79	4.86	4.55	3.41	4.12	3.44	3.29	3.23	3.27	3.23	3.16	3.16	2.89	5.90	5.74	6.25	6.66
H_2S in Retort Gas, mole%	0.50	0.63	1.80	0.47	1.44	0.43	0.87	(a)	(a)	(a)	(a)	(a)	3.21	5.34	(a)	(a)	1.51
Bed Height, ft	3.71	3.93	3.79	4.14	3.43	4.00	4.29	4.36	4.14	3.76	3.54	3.72	3.72	3.96	4.19	3.88	3.65
Solids Residence Time, min.	13.67	13.48	13.31	10.90	9.03	10.53	11.29	11.48	10.90	10.28	9.68	10.17	10.17	12.91	13.66	12.65	11.90
Gas Velocity, ft/sec	5.54	5.59	5.94	5.96	5.41	5.37	5.12	5.55	5.09	4.92	4.21	4.49	4.53	7.20	6.84	7.13	6.34
Gas Residence Time in Bed, sec.	0.67	0.70	0.64	0.69	0.63	0.75	0.84	0.79	0.81	0.76	0.84	0.83	0.82	0.55	0.61	0.54	0.58
Carbonate Decomposition, %														74.8			
Organic Carbon Combustion Efficiency, %			95.82		100.00		100.00							68.05			
Ca/S Mole Ratio														6.20			
Flue Gas Analyzers																	
XS O_2, mole %	6.0	3.0	5.0	6.1	4.5	4.0	4.3	5.8	4.0	2.0	0.5	1.75	2.5	3.9	2.0	1.4	0.2
CO, mole %	0.08	0.35	0.09	0.09	0.10	0.17	0.27	0.24	0.30	0.75	1.44	0.53	0.39	0.06	0.10	0.08	0.45
SO_2, ppmv	5	2	2	1	1	2	2	2	2	5	6	6	3	2	1	1.5	3
NO_x, ppmv	670	360	560	560	400	360	360	400	310	200	160	160	200	260	240	210	160

(a) No retort gas sample taken.
(b) Bad retort gas sample.
(c) Shale dust in retort gas sample absorbed H_2S.
(d) Natural gas and H_2S fed to combustor.
NA No analysis.

(continued)

TABLE A-2. (continued)

	Single Stage Combustion												
Test Number	7C	7D	8	9	10P	11A	14	16	17A	17B	17C	18	20P
Temperature, °F													
Inlet Gas Heater	1396	1394	1395	1437	1454	1493	1540	1587	1307	1376	1257	1242	1577
Fluid Bed	1508	1415	1441	1363	1339	1428	1134	1127	1299	1376	1403	1367	1295
Freeboard	1471	1523	1496	1423	1440	1441	1309	1273	1319	1414	1466	1474	1426
Baghouse	339	403	381	284	361	353	299	331	383	374	392	395	344
Stack	250	250	254	180	225	210	175	220	260	275	295	295	248
Pressure, Inches Water													
Fluid Bed (6 in. above distributor)	77	86	88	84	81	87	70	68	80	81	82	93	66
Freeboard	37	50	41	42	31	25	30	20	30	35	40	45	22
Flow Rates to Combustor													
Retorted Solids, lb/hr	2535	2587	2603	2907	3040	2510	3581	3615	3482	3504	3535	3525	3400
Raw Shale, lb/hr	0	0	0	0	0	0	0	0	133.1	133.1	133.1	0	0
Retort Gas, SCFM	5.62	4.93	4.60	4.09	3.89	4.45	5.50	4.73	0	0	0	4.87	5.11
H_2S in Retort Gas, mole%	(b)	3.77	9.28	0.81	(a)	(c)	3.85	(a)	--	--	--	(c)	(a)
Bed Height, ft	3.58	3.27	4.12	3.50	4.07	4.78	3.46	4.06	4.35	4.03	3.73	4.06	3.88
Solids Residence Time, min.	11.67	10.41	13.43	10.32	12.00	18.72	8.07	8.74	10.27	9.51	8.81	9.59	9.16
Gas Velocity, ft/sec	7.05	7.14	6.43	6.16	5.36	4.89	4.21	4.11	4.79	5.69	6.13	5.96	4.81
Gas Residence Time in Bed, sec.	0.51	0.46	0.64	0.57	0.76	0.98	0.82	0.99	0.91	0.71	0.61	0.78	0.81
Carbonate Decomposition, %			83.3				45.5			57.4			
Organic Carbon Combustion Efficiency, %			100.00			82.33	57.51		79.72	89.79	95.31	91.28	
Ca/S Mole Ratio			7.27				6.29			7.84			
Flue Gas Analyzers													
XS O_2, mole %	3.5	5.3	3.1	4.5	0.2	0	0.15	0.10	0.1	0.1	0.5	1.5	0
CO, mole %	0.075	0.07	0.08	0.08	0.51	0.93	1.80	0.85	1.29	1.20	1.13	0.36	0.81
SO_2, ppmv	2	1	2	1	1	4	25	14	38	35	22	6	12
NO_x, ppmv	440	550	420	NA	340	240	120	80	200	200	220	380	440

(a) No retort gas sample taken.
(b) Bad retort gas sample.
(c) Shale dust in retort gas sample absorbed H_2S.
(d) Natural gas and H_2S fed to combustor.
NA No analysis.

(continued)

TABLE A-2. (continued)

	Two Stage Combustion													
Test Number	T10	T11	T11B	T11C	T11D	T12	T12A	T13	T15	T17D	T19A	T19B	T19C	T20
Temperature, °F														
Inlet Gas Heater	1488	1295	1498	1481	1483	1454	1454	1438	617	1254	1302	1427	1562	1747
Fluid Bed	1363	1494	1366	1384	1354	1424	1429	1447	1170	1370	1245	1200	1227	1268
Freeboard	1435	1593	1457	1462	1412	1499	1496	1478	1430	1477	1461	1409	1509	1540
Baghouse	303	392	334	376	364	376	332	302	355	402	299	290	330	374
Stack	230	260	210	242	252	260	245	250	207	305	240	246	248	260
Pressure, Inches Water														
Fluid Bed (6 in. above distributor)	80	96	96	96	90	90	87	83	66	102	87	77	75	75
Freeboard	34	50	36	44	44	40	41	38	17	60	39	34	30	34
Flow Rates to Combustor														
Retorted Solids, lb/hr	3013	2921	2510	2530	2511	2867	2703	2728	3311	3490	3454	3454	3454	3400
Raw Shale, lb/hr	0	0	0	0	0	0	0	0	0	133.1	94.7	94.7	94.7	0
Retort Gas, SCFM	3.87	6.03	4.53	4.14	3.43	5.79	6.23	4.40	6.36	0	0	0	0	5.10
H_2S in Retort Gas, mole%	3.94	1.18	(c)	3.90	4.11	(c)	(a)	(d)	1.98	--	--	--	--	(b)
Bed Height, ft	3.79	3.79	4.64	4.09	3.67	3.95	3.74	3.71	4.27	3.73	4.06	3.69	3.83	3.65
Solids Residence Time, min.	11.18	11.64	18.17	15.61	14.01	12.57	12.98	12.43	10.83	8.81	9.95	9.05	9.39	8.62
Gas Velocity, ft/sec	5.41	5.91	4.62	4.74	4.88	6.03	6.17	6.05	3.78	5.29	4.62	4.30	4.41	4.07
Gas Residence Time in Bed, sec.	0.70	0.64	1.01	0.86	0.75	0.65	0.61	0.61	1.13	0.70	0.88	0.86	0.87	0.90
Carbonate Decomposition, %		81.7						80.2					55.3	
Organic Carbon Combustion Efficiency, %	96.63	100.00	71.10	60.18	77.71	76.56		80.93					88.88	85.80
Ca/S Mole Ratio		7.48				8.33		7.59					10.25	
Flue Gas Analyzers														
XS O_2, mole %	2.9	3.0	2.0	4.0	6.25	3.2	4.1	4.1	4.5	3.5	NA	1.0	2.6	2.0
CO, mole %	0.11	0.12	0.62	0.06	0.05	0.05	0.11	0.03	0.14	1.19	0.17	0.65	0.27	0.05
SO_2, ppmv	1	2	2	2	2	3	2	2	4	14	14	23	11	7
NO_x, ppmv	290	280	320	360	480	500	500	560	340	160	320	160	160	280

(a) No retort gas sample taken.
(b) Bad retort gas sample.
(c) Shale dust in retort gas sample absorbed H_2S.
(d) Natural gas and H_2S fed to combustor.
NA No analysis.

TABLE A-3. PROPERTIES OF RETORTED SOLIDS FEED TO COMBUSTOR

Test Number	2	4	6	7	8	10	11	11A	11B	11C	11D	12	13	14	17A	17B	17C	18	19C	20
Elemental Analysis, wt %																				
Mineral Carbon	0.78	1.11	1.48	0.58	0.82	0.90	0.83	1.10	1.15	1.16	1.39	1.20	1.06	1.58	1.43	1.13	1.17	0.92	1.56	1.63
Organic Carbon	0.52	0.49	0.37	0.59	0.54	0.58	0.55	0.96	0.89	0.82	0.97	0.96	0.68	0.82	0.70	0.75	0.57	0.54	0.68	0.75
Hydrogen	0.02	0.02	0.02	0.02	0.01	0.04	0.02	0.07	0.12	0.12	0.12	0.10	0.07	0.13	0.07	0.06	0.03	0.02	0.08	0.06
Nitrogen	0.04	0.05	0.05	0.05	0.06	0.06	0.06	0.08	0.13	0.15	0.14	0.12	0.14	0.14	0.11	0.08	0.06	0.04	0.06	0.08
Sulfur	0.38	0.60	0.79	0.59	0.52	0.54	0.53	0.49	0.44	0.49	0.48	0.54	0.51	0.86	0.73	0.66	0.49	0.50	0.52	0.58
Ash Analysis, wt %																				
Dolomite																				
$MgCO_3$				0.0	0.0		0.0					0.0	0.0	0.0		0.0			0.0	
$CaCO_3$				0.0	0.0		0.0					2.2	1.2	3.3		0.5			3.7	
Total				0.0	0.0		0.0					2.2	1.2	3.3		0.5			3.7	
Calcite																				
$CaCO_3$				4.8	6.8		6.5					7.8	7.7	9.8		8.9			9.3	
Total $CaCO_3$				4.8	6.8		6.5					10.0	8.9	13.1		9.4			13.0	
Ca, wt %				5.05	5.48		4.87					6.04	5.67	7.00		6.75			6.66	
Mg, wt %				1.51	1.56		1.37					1.76	1.58	1.86		1.83			1.78	
Screen Size, Standard Mesh, wt %																				
+ 4				0.51	0.87		0.71					0.30	0.60	0.54		0.37			0.96	
-4 + 8				10.09	10.29		9.77					6.93	8.85	8.16		7.91			14.09	
-8 + 12				12.16	12.19		8.74					7.76	8.52	6.87		5.94			10.79	
-12 + 20				34.67	35.77		33.70					29.93	32.88	26.49		25.48			27.65	
-20 + 40				36.58	35.66		41.36					42.20	43.49	48.41		51.34			40.81	
-40 + 80				2.31	2.82		2.27					3.95	2.81	6.78		4.31			3.03	
-80				3.68	2.40		3.45					8.93	2.85	2.75		4.65			2.67	

TABLE A-4. PROPERTIES OF COMBUSTED SHALE (HEAT CARRIER) FROM COMBUSTOR

Test Number	2	4	6	7	8	10	11	11A	11B	11C	11D	12	13	14	17A	17B	17C	18	19C	20
Elemental Analysis, wt %																				
Mineral Carbon	0.82	0.82	1.20	0.33	0.33	0.36	0.35	0.57	0.50	0.32	0.47	0.52	0.41	1.32	0.96	1.06	0.62	0.43	1.18	1.45
Organic Carbon	0.00	0.00	0.00	0.22	0.00	0.00	0.00	0.00	0.21	0.30	0.21	0.21	0.11	0.22	0.10	0.06	0.00	0.00	0.12	0.11
Hydrogen	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.04	0.04	0.04	0.06	0.04	0.06	0.00	0.00	0.00	0.00	0.02	0.02
Nitrogen	0.02	0.02	0.04	0.03	0.00	0.02	0.00	0.02	0.10	0.12	0.08	0.10	0.10	0.10	0.04	0.02	0.01	0.01	0.02	0.02
Sulfur	0.44	0.55	0.78	0.60	0.53	0.41	0.44	0.41	0.43	0.41	0.43	0.44	0.45	0.84	0.75	0.66	0.46	0.47	0.54	0.51
Ash Analysis, wt %																				
Dolomite																				
$MgCO_3$				0.0	0.0		0.0					0.0	0.0	0.0		0.0			0.0	
$CaCO_3$				0.0	0.0		0.0					0.0	0.0	1.6		0.0			1.0	
Total				0.0	0.0		0.0					0.0	0.0	1.6		0.0			1.0	
Calcite																				
$CaCO_3$				2.8	2.8		2.9					4.3	3.4	9.4		8.8			8.8	
Total $CaCO_3$				2.8	2.8		2.9					4.3	3.4	11.0		8.8			9.8	
Ca, wt %				5.88	5.52		4.60					5.18	5.02	6.94		7.23			6.31	
Mg, wt %				1.71	1.55		1.28					1.43	1.34	1.92		1.97			1.69	
Screen Size, Standard Mesh, wt %																				
+ 4				0.70	1.10		0.98					0.80	0.52	0.46		0.57			0.46	
-4 + 8				17.02	22.01		13.01					13.61	15.03	9.14		15.94			12.58	
-8 + 12				13.66	13.65		9.22					10.11	9.74	6.94		7.75			11.03	
-12 + 20				35.65	31.78		32.94					31.45	31.49	26.86		24.09			29.54	
-20 + 40				31.46	29.58		40.86					41.34	40.75	49.58		47.57			43.29	
-40 + 80				0.80	0.88		1.59					1.55	1.09	5.72		2.51			2.35	
-80				0.71	1.02		1.40					1.14	1.38	1.30		1.57			0.75	

TABLE A-5. PROPERTIES OF COMBUSTED FINES (BAGHOUSE ASH) FROM COMBUSTOR

Test Number	2	4	6	7	8	10	11	11A	11B	11C	11D	12	13	14	17A	17B	17C	18	19C	20
Elemental Analysis, wt %																				
Mineral Carbon	2.59	3.70	3.85	2.22	0.97	2.72	0.77	2.66	2.85	2.45	2.59	1.13	0.76	4.72	4.65	3.39	2.79	3.10	3.03	2.79
Organic Carbon	0.15	0.00	0.00	0.02	0.00	0.16	0.00	1.10	0.49	0.47	0.26	0.31	0.28	1.53	1.45	0.71	0.40	0.36	0.20	0.09
Hydrogen	0.04	0.04	0.03	0.02	0.00	0.03	0.00	0.12	0.12	0.14	0.12	0.10	0.11	0.24	0.20	0.07	0.07	0.08	0.09	0.06
Nitrogen	0.14	0.15	0.18	0.12	0.09	0.15	0.10	0.24	0.18	0.23	0.20	0.22	0.19	0.33	0.26	0.16	0.13	0.12	0.16	0.11
Sulfur	1.23	1.13	1.09	1.45	1.72	1.42	1.46	1.27	1.13	1.25	1.23	1.43	1.81	1.08	0.99	1.13	1.15	1.12	1.01	1.08
Ash Analysis, wt %																				
Dolomite																				
$MgCO_3$				0.0	0.0		0.0					0.0	0.0	5.8		0.0			0.0	
$CaCO_3$				0.0	0.0		0.0					0.0	0.0	15.2		8.8			7.6	
Total				0.0	0.0		0.0					0.0	0.0	21.0		8.8			7.6	
Calcite																				
$CaCO_3$				18.5	8.1		6.4					9.4	6.3	17.2		19.5			17.7	
Total $CaCO_3$				18.5	8.1		6.4					9.4	6.3	32.4		28.3			25.3	
Ca, wt %				14.50	15.10		16.00					15.45	16.50	13.00		14.70			13.85	
Mg, wt %				4.17	4.11		4.24					4.48	4.28	3.70		4.19			4.11	
Screen Size, Standard Mesh, wt %																				
+ 4				0.00	0.00		0.00					0.00	0.00	0.00		0.00			0.00	
-4 + 8				0.02	0.00		0.00					0.00	0.00	0.00		0.01			0.00	
-8 + 12				0.06	0.00		0.00					0.00	0.00	0.00		0.02			0.00	
-12 + 20				0.25	0.00		0.01					0.03	0.01	0.05		0.02			0.02	
-20 + 40				0.22	0.10		0.11					0.07	0.09	0.08		0.02			0.03	
-40 + 80				0.39	0.22		0.36					0.18	3.95	0.10		0.03			0.06	
-80				99.06	99.68		99.52					99.72	95.95	99.77		99.90			99.89	
-80 Mesh In Microns, wt %																				
-176 + 125				0.0	0.0		0.0					0.0	0.0	0.0		0.0			0.0	
-125 + 88				0.0	0.0		0.0					0.0	0.0	0.0		0.0			0.0	
-88 + 62				0.0	0.0		0.0					0.0	0.0	0.0		0.0			0.0	
-62 + 44				0.0	0.0		0.0					0.0	0.0	0.0		0.0			0.0	
-44 + 31				0.0	0.4		0.0					0.0	0.0	0.0		0.0			0.0	
-31 + 22				10.1	8.1		7.2					6.5	7.8	4.4		7.1			7.3	
-22 + 16				9.0	8.1		7.6					6.5	7.8	9.1		7.2			6.2	
-16 + 11				13.1	8.0		8.8					4.6	8.7	5.2		6.1			9.7	
-11 + 7.8				21.9	19.6		15.7					14.8	21.0	13.3		15.2			18.1	
-7.8 + 5.5				17.0	19.0		19.2					17.8	20.3	20.8		17.2			19.4	
-5.5 + 3.9				12.8	14.6		17.3					18.3	14.7	18.5		18.0			16.6	
-3.9 + 2.8				7.9	10.7		11.0					14.4	9.7	13.5		13.5			10.9	
-2.8 + 1.9				8.2	11.5		13.2					17.1	10.0	15.2		15.7			11.8	
Mean Diameter, microns				10.37	9.32		8.76					7.92	9.28	7.89		8.30			8.81	

TABLE A-6. ELEMENTAL ANALYSIS OF SELECTED SOLIDS BY X-RAY FLUORESCENCE

	Test Number 7				Test Number 12			Test Number 19			
	Raw Shale	Retorted Solids	Heat Carrier	Baghouse Ash	Retorted Solids	Heat Carrier	Baghouse Ash	Raw Shale	Retorted Solids	Heat Carrier	Baghouse Ash
Element, wt %											
Silica	17.4	26.0	29.2	24.9	25.2	28.1	24.5	17.9	24.4	24.7	25.1
Calcium	12.6	7.7	8.5	15.2	8.9	8.4	15.0	13.8	9.6	9.2	15.8
Iron	6.5	10.7	11.1	6.6	10.1	11.2	6.8	5.9	9.8	9.9	6.5
Aluminum	4.2	7.0	8.0	5.3	6.9	7.6	5.1	4.0	6.3	6.1	5.3
Magnesium	1.9	1.5	1.8	3.4	1.7	1.7	3.7	1.8	1.7	1.5	3.6
Potassium	1.8	2.6	2.6	2.2	2.3	2.6	2.2	1.8	2.2	2.3	2.2
Sulfur(a)	0.86	0.59	0.60	1.45	0.54	0.44	1.43	0.75	0.52	0.54	1.01
Titanium	0.08	0.15	0.15	0.09	0.14	0.15	0.05	0.08	0.13	0.14	0.09
Strontium	0.03	0.03	0.04	0.04	0.03	0.03	0.04	0.04	0.03	0.03	0.04
Barium	ND(b)	0.004	0.004	ND	ND	0.007	ND	ND	0.004	0.007	ND
Arsenic(c)	0.005	0.005	0.005	ND	ND	ND	ND	ND	0.005	0.005	ND
Mercury(c)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Cadmium(c)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Sodium(d)	4	4	4	4	4	4	4	4	4	4	4
Others	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

(a) From separate sulfur determination using x-ray fluorescence.
(b) ND = Not detected.
(c) Detection limit = 0.005%.
(d) Detection limit = 4%.

TABLE A-7. ANALYSIS OF NATURAL GAS AND RETORT GAS USED IN COMBUSTOR TESTS

	Natural	Retort Gas																
Test Number	Gas	1	1A	2	3	4	5	6	6A	6B	6C	6D	6E	6F	7	7A	7AA	7B
Component, Mole % (Normalized)																		
$Ar+O_2$	1.41				0.13			0.20						0.19				
N_2	9.41	Sulfur	25.29	29.69	36.14	25.75	45.56	42.10	No	No	No	No	No	50.03	24.42	No	No	28.20
H_2		Analysis	19.79	17.09	19.20	21.13	17.60	18.76	Sample	Sample	Sample	Sample	Sample	16.02	15.51	Sample	Sample	16.08
CO		Only	2.32	1.81	2.06	2.05	1.64	1.36	Taken	Taken	Taken	Taken	Taken	1.00	2.14	Taken	Taken	1.89
CO_2	1.55		14.65	13.79	13.44	14.28	12.00	11.94						7.55	10.13			10.71
H_2S		0.50	0.63	1.80	0.47	1.44	0.43	0.87						3.21	5.34			1.51
C_1	78.88		12.86	12.67	10.24	12.67	8.33	8.90						7.50	14.60			14.13
C_2	7.40		5.21	4.92	4.14	4.80	3.28	3.45						3.12	4.98			5.11
$C_2^=$			4.90	5.15	3.12	4.47	1.44	1.79						1.69	8.25			8.27
C_3	1.18		2.50	2.19	2.19	2.24	1.87	1.89						1.66	1.63			1.66
$C_3^=$			4.59	4.58	3.30	4.27	2.07	2.34						2.14	6.27			6.12
$i\text{-}C_4$	0.05		0.14	0.13	0.13	0.12	0.12	0.13						0.10	0.10			0.09
$n\text{-}C_4$	0.11		0.88	0.73	0.85	0.80	0.82	0.79						0.76	0.46			0.40
$C_4^=$			3.10	2.84	2.30	2.90	1.68	1.81						1.66	3.34			3.09
$i\text{-}C_5$	0.01		0.77	0.70	0.50	0.70	0.39	0.42						0.37	0.34			0.86
$n\text{-}C_5$			0.42	0.30	0.41	0.39	0.44	0.44						0.43	0.19			0.13
$C_5^=$			1.52	1.09	1.30	1.48	0.91	0.87						0.84	1.04			0.60
C_6^+			0.43	0.53		0.51	1.34	1.94						1.74	1.26			1.16
Total	100.00		100.00	100.00	100.00	100.00	100.00	100.00						100.00	100.00			100.00
Mole Weight	19.27	--	27.46	27.73	26.81	26.93	27.31	27.40						27.43	27.94			27.56
H_2S and COS Spike	--	No	No	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes

(continued)

TABLE A-7 (continued)

	Retort Gas																
Test Number	7C	7D	8	9	10P	10	11	11A	11B	11C	11D	12	12A	13	14	15	16
Component, Mole % (Normalized)																	
$Ar+O_2$		0.16	0.10	15.19			0.23	1.07	0.37		0.08	0.56		No Sample Taken Natural Gas and H_2S injected rather than retort gas and H_2S	0.11	16.21	
N_2	Bad Sample	31.61	30.18	63.19	No Sample Taken	35.96	28.63	54.01	57.09	22.74	27.86	46.67	No Sample Taken		41.05	60.97	No Sample Taken
H_2		17.67	15.65	5.91		16.36	18.33	13.27	16.50	22.16	20.12	16.45			19.39	3.74	
CO		1.70	1.30	0.47		1.40	2.25	1.25	1.62	2.32	2.19	1.60			1.56	0.19	
CO_2		11.67	9.46	4.13		10.87	9.48	9.51		14.50	14.20	7.40			12.36	2.64	
H_2S		3.77	9.28	0.81		3.94	1.16			3.90	4.11				3.05	1.98	
C_1		11.82	11.00	3.87		10.57	14.29	7.38	9.09	12.81	11.90	9.36			7.99	2.09	
$C_2^=$		4.57	4.42	1.51		4.01	4.90	2.81	3.55	5.12	4.91	3.70			3.33	7.05	
C_2		5.72	5.51	1.56		4.22	7.94	2.41	2.91	3.94	3.53	4.16			1.34	0.44	
$C_3^=$		1.84	1.83	0.65		1.84	1.61	1.37	1.85	2.59	2.51	1.67			1.89	0.46	
C_3		4.58	4.53	1.30		3.79	5.87	2.28	2.52	3.97	3.70	3.55			2.01	0.59	
$i\text{-}C_4$		0.09	0.10			0.11	0.09	0.08	0.11	0.17	0.16	0.10			0.14		
$n\text{-}C_4$		0.58	0.67	0.21		0.69	0.40	0.47	0.61	1.01	0.96	0.53			0.87	0.20	
$C_4^=$		2.51	2.65	0.64		2.45	2.96	1.42	1.64	2.64	2.42	2.19			1.66	0.32	
$i\text{-}C_5$		0.64	0.69	0.19		0.66	0.80	0.49	0.40	0.64	0.56	0.59			0.39	0.07	
$n\text{-}C_5$		0.19	0.25	0.06		0.30	0.13	0.24	0.27	0.42	0.36	0.23			0.44	0.06	
$C_5^=$		0.69	0.90	0.23		1.00	0.65	0.62	0.60	1.07	0.84	0.73			0.91	1.19	
C_6^+		0.19	1.48			2.23	0.26	0.52	0.07			0.49			0.72		
Total		100.00	100.00	100.00		100.00	100.00	100.00	100.00	100.00	100.00	100.00			100.00	100.00	
Mole Weight		26.82	28.36	28.10		28.45	26.14	27.29	24.64	26.37	26.73	26.43			26.82	28.44	
H_2S and COS Spike	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Comments				Retort gas diluted with air when blower suction developed negative pressure				Shale dust in sample absorbed H_2S	Shale dust in sample absorbed H_2S and CO_2			Shale dust in sample absorbed H_2S				Retort gas with air when blower suction developed negative pressure	

(continued)

TABLE A-7 (continued)

	Retort Gas																	
Test Number	7C	7D	8	9	10P	10	11	11A	11B	11C	11D	12	12A	13	14	15	16
Component, Mole % (Normalized)																	
$Ar+O_2$		0.16	0.10	15.19			0.23	1.07	0.37		0.08	0.58		No Sample Taken Natural Gas and H_2S injected rather than retort gas and H_2S	0.11	16.21	
H_2	Bad Sample	31.61	30.18	63.19	No Sample Taken	35.56	28.63	54.81	57.89	22.74	27.86	46.67	No Sample Taken		41.05	69.97	No Sample Taken
N_2		17.67	15.65	5.91		16.36	18.33	13.27	16.50	22.16	20.12	16.45			19.39	3.74	
CO		1.70	1.30	0.47		1.40	2.25	1.25	1.62	2.32	2.19	1.60			1.56	0.19	
CO_2		11.67	9.46	4.13		10.87	9.48	9.51		14.50	14.20	7.40			12.35	2.64	
H_2S		3.77	9.28	0.81		3.94	1.18			3.90	4.11				3.85	1.98	
C_1		11.82	11.00	3.87		10.57	14.29	7.38	9.09	12.81	11.50	9.36			7.99	2.09	
C_2		4.57	4.42	1.51		4.01	4.90	2.81	3.55	5.12	4.91	3.70			3.33	0.85	
C_2^-		5.72	5.51	1.56		4.22	7.94	2.41	2.91	3.94	3.53	4.16			1.34	0.44	
C_3		1.84	1.83	0.65		1.84	1.61	1.37	1.85	2.59	2.51	1.67			1.89	0.46	
C_3^-		4.58	4.53	1.38		3.79	5.87	2.28	2.52	3.97	3.70	3.55			2.01	0.59	
i-C_4		0.09	0.10			0.11	0.09	0.08	0.11	0.17	0.16	0.10			0.14		
n-C_4		0.58	0.67	0.21		0.69	0.40	0.47	0.61	1.01	0.95	0.53			0.87	0.20	
C_4^-		2.51	2.65	0.64		2.45	2.96	1.42	1.64	2.64	2.42	2.19			1.66	0.32	
i-C_5		0.64	0.69	0.19		0.66	0.80	0.49	0.40	0.64	0.56	0.59			0.39	0.07	
n-C_5		0.19	0.25	0.06		0.30	0.13	0.24	0.27	0.42	0.36	0.23			0.44	0.06	
C_5^-		0.69	0.90	0.23		1.00	0.65	0.62	0.60	1.07	0.84	0.73			0.91	1.19	
C_6^+		0.19	1.48			2.23	0.26	0.52	0.07			0.49			0.72		
Total		100.00	100.00	100.00		100.00	100.00	100.00	100.00	100.00	100.00	100.00			100.00	100.00	
Mole Weight		26.82	28.36	28.10		28.45	26.14	27.29	24.64	26.37	26.73	26.43			26.82	28.44	
H_2S and COS Spike	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Comments				Retort gas diluted with air when blower suction developed negative pressure				Shale dust in sample absorbed H_2S	Shale dust in sample absorbed H_2S and CO_2			Shale dust in sample absorbed H_2S				Retort gas with air when blower suction developed negative pressure	

(continued)

TABLE A-7 (continued)

	Retort Gas									
Test Number Component, Mole % (Normalized)	17A	17B	17C	17D	18	19A	19B	19C	20P	20
Ar+O_2	No Retort Gas to Combustor	No Retort Gas to Combustor	No Retort Gas To Combustor	No Retort Gas To Combustor	2.35	No Retort Gas to Combustor	No Retort Gas to Combus tor	No Retort Gas to Combustor	No Sample Taken	Bad Sample
N_2					23.13					
H_2					23.96					
CO					2.28					
CO_2					15.08					
H_2S										
C_1					11.74					
C_2					4.83					
C_2^-					4.47					
C_3					2.33					
C_3^-					4.14					
1-C_4					0.12					
n-C_4					0.78					
C_4^-					2.65					
1-C_5					0.71					
n-C_5					0.37					
C_5^-					1.06					
C_6^+										
Total					100.00					
Mole Weight					25.88					
H_2S and COS Spike	No	No	No	No	Yes	No	No	No	No	No
Comments					Shale dust in sample absorbed H_2S					Shale dust in sample absorbed H_2S and interfered with analysis

TABLE A-6. COMBUSTOR FLUE GAS COMPOSITION AND FLOW RATES

	Single Stage Combustion																
Test Number	1	1A	2	3	4	5	6	6A	6B	6C	6D	6E	6F	7	7A	7AA	7B
Fluid Bed Temp.°F	1344	1359	1367	1269	1250	1145	1179	1167	1174	1147	1147	1179	1179	1558	1487	1553	1552
Continuous Analyzers																	
O_2, mole %	6.0	3.0	5.0	6.1	4.5	4.0	4.3	5.8	4.0	2.0	0.5	1.75	2.5	3.9	2.0	1.4	0.2
CO, mole %	0.08	0.35	0.09	0.09	0.10	0.17	0.27	0.24	0.30	0.75	1.44	0.53	0.39	0.06	0.10	0.08	0.45
SO_2, ppm	5	2	2	1	1	2	2	2	2	5	6	6	3	2	1	1.5	3
NO_x, ppm	670	360	560	560	400	360	360	400	310	200	160	160	200	260	240	210	160
Gas Chromatographic Analysis, Mole % (Dry, Normalized)																	
Ar	No	0.98	0.97	0.97	0.97	Air In	0.97	No	0.96	No	No	No	0.98	0.97	0.95	No	0.97
O_2	Sample	0.62	5.38	6.18	3.91	Sample	5.12	Sample	4.30	Sample	Sample	Sample	2.08	4.27	1.57	Sample	0.88
N_2	Taken	81.77	81.45	81.12	81.13		81.23	Taken	80.69	Taken	Taken	Taken	82.18	80.56	79.46	Taken	80.73
CO																	0.16
CO_2		16.63	12.20	11.73	13.99		12.68		14.05				14.76	14.20	18.02		17.26
C_1																	
C_3																	
C_6																	
TOTAL		100.00	100.00	100.00	100.00		100.00		100.00				100.00	100.00	100.00		100.00
Trace Hydrocarbons by Flame Ionization Detector (as butane), ppm		598	61	51	66		88		156				NA	89	250		729
Mole Weight (Dry)	30.80(a)	30.41	30.29	30.25	30.52	29.95(a)	30.36	30.40(a)	30.54	30.55(a)	30.55(a)	30.55(a)	30.57	30.57	31.07	31.00(a)	30.92
Moisture Content, Vol %(b)	27.31	32.70	23.97	14.94	20.30	23.97	19.41	19.88	20.98	21.38	33.46	37.06	29.80	22.11	21.24	24.40	22.31
Mole Weight (Wet)(b)	27.31	26.63	27.35	28.42	27.98	27.09	27.97	27.94	27.91	27.87	26.35	25.91	26.83	27.80	28.30	27.83	28.04
Flow Rates (Wet)																	
SCFM	202.2	217.1	207.1	203.4	190.6	229.3	187.1	212.5	193.4	188.6	183.6	206.0	184.5	224.9	225.4	234.9	191.8
lb/hr	873.1	914.2	895.2	913.8	843.2	981.9	827.1	938.4	853.6	830.9	765.0	843.9	782.7	966.4	1000.6	1033.9	850.6

(a) Estimated mole weight.
(b) Estimated by trial and error technique.
NA No analysis.

(continued)

TABLE A-8. (continued)

	Single Stage Combustion												
Test Number	7C	7D	8	9	10P	11A	14	16	17A	17B	17C	18	20P
Fluid Bed Temp.°F	1508	1415	1441	1363	1339	1428	1134	1127	1299	1376	1403	1367	1295
Continious Analyzers													
O2, mole %	3.5	5.3	3.1	4.5	0.2	0	0.15	0.10	0.1	0.1	0.5	1.5	0
CO, mole %	0.075	0.07	0.08	0.08	0.51	0.93	1.80	0.85	1.29	1.20	1.13	0.36	0.81
SO_2, ppmv	2	1	2	1	1	4	25	14	38	35	22	6	12
NO_x, ppmv	440	550	420	NA	340	240	120	80	200	200	220	380	440
Gas Chromatographic Analysis, Mole % (Dry, Normalized)													
Ar	0.96	0.95	0.95	Air	0.98	0.96	0.99	No	0.97	0.96	0.95	Air	No
O_2	3.74	2.68	4.33	In	1.42	0.51	0.70	Sample	0.20	0.68	0.92	In	Sample
N_2	79.87	79.42	79.34	Sample	81.97	80.34	82.08	Taken	80.80	79.80	79.25	Sample	Taken
CO		0.03			0.24	0.84	1.63		0.67	0.61	0.46		
CO_2	15.43	16.92	15.38		15.39	17.10	14.05		16.79	17.83	18.42		
C_1						0.25	0.55		0.38	0.12			
C_3									0.15				
C_5									0.04				
TOTAL	100.00	100.00	100.00		100.00	100.00	100.00		100.00	100.00	100.00		
Trace Hydrocarbons by Flame Ionization Detector (as butane), ppmv	111	NA	55		806	2976	5900		8465	3248	1249		
Mole Weight (Dry)	30.74	30.94	30.76	30.70(a)	30.65	30.85	30.34	30.30(a)	30.81	30.99	31.11	30.15(a)	30.49(a)
Moisture Content, Vol %(b)	22.58	18.64	23.87	25.20	28.32	42.52	35.35	27.30	31.10	29.62	26.34	27.95	26.11
Mole Weight (Wet)(b)	27.87	28.53	27.72	27.50	27.08	25.40	25.98	26.95	26.83	27.15	27.66	26.76	27.23
Flow Rates (Wet)													
SCFM	226.4	238.8	223.8	229.3	197.4	216.9	190.0	162.1	193.4	220.4	227.7	231.5	170.7
lb/hr	997.3	1077.0	980.8	997.0	844.9	870.9	780.7	690.8	820.4	945.9	996.0	979.6	735.1

(a) Estimated mole weight.
(b) Estimated by trial and error technique.
NA No analysis.

(continued)

TABLE A-8. (continued)

	Two Stage Combustion													
Test Number	**10**	**11**	**11B**	**11C**	**11D**	**12**	**12A**	**13**	**15**	**17D**	**19A**	**19B**	**19C**	**20**
Fluid Bed Temp.°F	1363	1494	1366	1384	1354	1424	1429	1447	1170	1370	1245	1200	1227	1268
Continuous Analyzers														
O_2, mole %	2.9	3.0	2.0	4.0	6.25	3.2	4.1	4.1	4.5	3.5	NA	1.0	2.6	2.0
CO, mole %	0.11	0.12	0.62	0.06	0.05	0.11	0.09	0.03	0.14	1.19	0.17	0.65	0.27	0.05
SO_2, ppmv	1	2	2	2	2	3	2	2	4	14	14	23	11	7
NO_x, ppmv	290	280	320	360	480	500	500	560	340	160	320	160	160	280
Gas Chromatographic Analysis, Mole % (Dry, Normalized)														
Ar	0.97	0.95	0.96	0.96	Air	0.96	0.95	0.95	Air	No	No	No	0.96	0.96
O_2	3.98	2.83	2.72	6.22	In	4.45	3.99	6.25	In	Sample	Sample	Sample	2.50	4.68
N_2	81.03	79.59	80.77	79.75	Sample	79.66	79.55	79.82	Sample	Taken	Taken	Taken	79.90	80.75
CO			0.07										0.54	
CO_2	14.02	16.63	15.48	13.07		14.93	15.51	12.98					16.10	13.61
C_1														
C_3														
C_5														
TOTAL	100.00	100.00	100.00	100.00		100.00	100.00	100.00					100.00	100.00
Trace Hydrocarbons by Flame Ionization Detector (as butane), ppmv	493	149	124	72		117	NA	76					380	52
Mole Weight (Dry)	30.53	30.90	30.71	30.46	30.50$^{(a)}$	30.69	30.76	30.45	30.30$^{(a)}$	31.00$^{(a)}$	30.80$^{(a)}$	30.80$^{(a)}$	30.80	30.49
Moisture Content, Vol %$^{(b)}$	16.40	14.53	19.84	7.91	7.36	0	0	0	15.48	27.08	19.28	16.38	16.23	18.00
Mole Weight (Wet)$^{(b)}$	28.48	29.03	28.19	29.48	29.58	30.69	30.76	30.45	28.40	27.76	28.33	28.70	28.73	28.25
Flow Rates (Wet)														
SCFM	209.4	235.0	205.9	223.8	229.2	214.2	216.2	216.6	156.9	252.9	231.2	211.2	210.8	208.3
lb/hr	942.9	1078.7	917.6	1043.1	1072.0	1039.4	1051.6	1042.6	704.5	1109.6	1035.5	958.5	957.5	930.4

(a) Estimated mole weight.
(b) Estimated by trial and error technique.
NA No analysis.

TABLE A-9. OVERALL MASS FLOW BALANCES

RUN NO.	1	1A	2	3	4	5	6	6A	6B	6C	6D
INPUTS,LB/HR											
RETORTED SOLIDS	2487.00	2662.00	2601.00	3404.00	3352.00	3395.00	3343.00	3345.00	3343.00	3158.00	3062.00
STEAM	156.80	178.50	179.80	138.90	153.00	122.50	127.80	135.50	128.50	147.30	172.40
AIR	683.40	679.90	730.30	802.00	702.90	784.60	695.60	788.30	700.70	676.70	564.70
NAT'L GAS	15.90	15.70	11.90	10.30	8.30	11.60	12.00	11.40	13.80	18.00	15.60
RETORT GAS	16.40	21.10	19.90	14.40	17.50	14.90	14.30	14.00	14.10	14.00	13.70
OVERFIRE AIR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PURGES	10.30	10.50	11.30	11.10	11.80	11.10	11.80	11.80	11.80	11.80	11.80
RAW SHALE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TOTAL INPUTS	3369.80	3567.70	3554.20	4380.70	4245.50	4339.70	4204.50	4306.00	4211.90	4025.80	3840.20
OUTPUTS, LB/HR											
HEAT CARRIER	2091.00	2247.00	2195.00	2927.00	2927.00	2927.00	2927.00	2927.00	2927.00	2718.00	2718.00
BAGHOUSE ASH	368.00	420.00	377.00	479.00	408.00	464.00	330.00	391.00	441.00	464.00	385.00
FLUE GAS	873.10	914.20	895.20	913.80	843.20	981.90	827.10	938.40	853.60	830.90	765.00
TOTAL OUTPUTS	3332.10	3581.20	3467.20	4319.80	4178.20	4372.90	4084.10	4256.40	4221.60	4012.90	3868.00
BALANCE CLOSURE,%	98.88	100.38	97.55	98.61	98.41	100.77	97.14	98.85	100.23	99.68	100.72

RUN NO.	6E	6R	7	7A	7AA	7B	7C	7D	8	9	10P
INPUTS,LB/HR											
RETORTED SOLIDS	3014.00	3014.00	2598.00	2620.00	2620.00	2620.00	2535.00	2587.00	2603.00	2907.00	3040.00
STEAM	148.10	148.10	137.00	139.30	136.30	139.40	152.90	133.20	135.30	154.20	143.00
AIR	600.90	600.90	803.30	803.30	803.30	679.20	795.70	879.70	768.80	767.20	656.60
NAT'L GAS	14.80	14.80	16.20	16.20	16.00	13.70	16.20	16.00	16.00	16.40	18.00
RETORT GAS	13.70	12.50	26.10	24.40	27.60	29.40	23.80	20.90	20.60	18.40	17.50
OVERFIRE AIR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PURGES	11.80	11.80	12.60	12.60	12.60	12.60	12.60	12.60	12.60	11.80	11.80
RAW SHALE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TOTAL INPUTS	3803.30	3802.10	3593.20	3615.80	3615.80	3494.30	3536.20	3649.40	3556.30	3875.00	3886.90
OUTPUTS, LB/HR											
HEAT CARRIER	2718.00	2718.00	2195.00	2195.00	2195.00	2195.00	2195.00	2247.00	2195.00	2613.00	2613.00
BAGHOUSE ASH	222.00	222.00	340.00	360.00	360.00	303.00	278.00	260.00	335.00	302.00	391.00
FLUE GAS	843.90	782.70	988.40	1008.60	1033.90	850.60	997.30	1077.00	980.80	997.00	844.90
TOTAL OUTPUTS	3783.90	3722.70	3523.40	3563.60	3588.90	3348.60	3470.30	3584.00	3510.80	3912.00	3848.90
BALANCE CLOSURE,%	99.49	97.91	98.06	98.56	99.26	95.83	98.14	98.21	98.72	100.95	99.02

(continued)

TABLE A-9 (continued)

RUN NO.	10	11	11A	11B	11C	11D	12	12A	13	14	15
INPUTS,LB/HR											
RETORTED SOLIDS	3013.00	2921.00	2510.00	2510.00	2530.00	2511.00	2867.00	2703.00	2728.00	3581.00	3311.00
STEAM	117.40	74.30	169.40	161.30	92.80	92.10	17.00	17.00	0.00	154.50	97.40
AIR	655.50	695.60	565.10	565.10	583.30	609.40	692.50	704.90	711.00	563.60	483.50
NAT'L GAS	18.00	13.40	15.60	15.50	16.40	16.70	17.10	17.20	16.40	14.10	6.90
RETORT GAS	17.40	24.90	18.80	18.90	17.20	14.50	26.10	28.00	16.00	23.30	28.60
OVERFIRE AIR	152.90	217.30	0.00	195.40	360.00	362.30	298.20	300.40	318.00	0.00	114.80
PURGES	11.80	11.80	11.80	11.80	11.80	11.80	11.80	11.80	11.80	11.70	11.80
RAW SHALE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TOTAL INPUTS	3986.00	3958.30	3290.70	3478.00	3611.50	3617.80	3929.70	3782.30	3801.20	4348.20	4054.00
OUTPUTS, LB/HR											
HEAT CARRIER	2613.00	2509.00	2038.00	2038.00	2091.00	2091.00	2509.00	2300.00	2300.00	3188.00	2822.00
BAGHOUSE ASH	368.00	347.00	387.00	444.00	423.00	399.00	381.30	430.70	360.00	357.00	335.00
FLUE GAS	942.90	1078.70	870.90	917.60	1043.10	1072.00	1039.40	1051.60	1042.60	780.70	704.50
TOTAL OUTPUTS	3923.90	3934.70	3295.90	3399.60	3557.10	3562.00	3929.70	3782.30	3702.60	4325.70	3861.50
BALANCE CLOSURE,%	98.44	99.40	100.16	97.75	98.49	98.46	100.00	100.00	97.41	99.48	95.25

RUN NO.	16	17A	17B	17C	17D	18	19A	19B	19C	20P	20
INPUTS,LB/HR											
RETORTED SOLIDS	3615.00	3482.00	3504.00	3535.00	3490.00	3525.00	3454.00	3454.00	3454.00	3400.00	3400.00
STEAM	134.50	162.70	162.70	157.50	168.70	151.70	156.50	152.70	115.10	135.40	115.50
AIR	540.10	616.60	711.00	764.90	704.90	751.30	631.10	583.40	583.40	575.10	501.30
NAT'L GAS	18.00	14.50	14.80	13.70	13.70	13.70	11.60	16.70	16.70	16.80	17.40
RETORT GAS	20.10	0.00	0.00	0.00	0.00	21.90	0.00	0.00	0.00	20.00	20.00
OVERFIRE AIR	0.00	0.00	0.00	0.00	137.30	0.00	228.90	228.90	228.90	0.00	285.30
PURGES	11.80	11.80	11.80	11.80	11.80	12.60	11.80	11.30	11.80	11.80	11.80
RAW SHALE	0.00	133.10	133.10	133.10	133.10	0.00	94.70	94.70	94.70	0.00	0.00
TOTAL INPUTS	4339.50	4420.70	4537.40	4616.00	4659.50	4476.20	4588.60	4541.70	4504.60	4159.10	4351.30
OUTPUTS, LB/HR											
HEAT CARRIER	3198.00	3031.00	3031.00	3031.00	3031.00	3031.00	3031.00	3031.00	3031.00	3031.00	3031.00
BAGHOUSE ASH	450.70	436.00	434.00	491.00	475.00	461.00	389.00	348.00	389.00	399.00	318.00
FLUE GAS	690.80	820.40	945.90	996.00	1109.60	979.60	1035.50	958.50	957.50	735.10	930.40
TOTAL OUTPUTS	4339.50	4287.40	4410.90	4518.00	4615.60	4471.60	4455.50	4337.50	4377.50	4165.10	4279.40
BALANCE CLOSURE,%	100.00	96.98	97.21	97.88	99.06	99.90	97.10	95.50	97.18	100.14	98.35

TABLE A-10. TOTAL CARBON BALANCES

RUN NO.	2	4	6	7	8	10	11	11A	11B	11C
INPUTS,LB/HR TOT C										
RETORTED SOLIDS	33.81	53.63	61.85	30.40	35.40	44.59	40.31	51.71	51.20	50.09
STEAM	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
AIR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NAT'L GAS	7.39	5.15	7.45	10.06	9.93	11.17	8.32	9.68	9.68	10.18
OVERFIRE AIR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
RETORT GAS	8.37	7.67	4.80	12.13	8.07	6.78	11.15	7.29	8.04	7.32
PURGES	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
RAW SHALE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TOTAL INPUTS	49.57	66.46	74.09	52.58	53.40	62.55	59.78	68.68	68.93	67.59
OUTPUTS, LB/HR TOT C										
HEAT CARRIER	18.00	24.00	35.12	12.07	7.24	9.41	8.78	11.62	14.47	12.96
BAGHOUSE ASH	10.33	15.10	12.71	7.62	3.25	10.60	2.67	14.55	14.83	12.35
FLUE GAS	41.54	40.30	36.31	47.25	49.73	46.58	63.43	43.02	48.72	51.11
TOTAL OUTPUTS	69.87	79.40	84.14	66.93	60.22	66.58	74.88	69.19	78.02	76.43
BALANCE CLOSURE,%	140.94	119.48	113.56	127.30	112.76	106.45	125.27	100.74	113.20	113.07

RUN NO.	11D	12	13	14	17A	17B	17C	18	19C	20
INPUTS,LB/HR TOT C										
RETORTED SOLIDS	59.26	61.93	47.47	85.94	74.17	65.88	61.51	51.47	77.37	80.92
STEAM	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
AIR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NAT'L GAS	10.37	10.61	10.18	8.75	9.00	9.19	8.50	8.50	10.37	10.80
OVERFIRE AIR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
RETORT GAS	5.63	11.03	6.76	6.95	0.00	0.00	0.00	8.53	0.00	7.79
PURGES	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
RAW SHALE	0.00	0.00	0.00	0.00	27.53	27.53	27.53	0.00	19.58	0.00
TOTAL INPUTS	75.25	83.57	64.41	101.65	110.69	102.59	97.54	68.50	107.32	99.51
OUTPUTS, LB/HR TOT C										
HEAT CARRIER	14.22	18.32	11.96	49.10	32.13	33.95	18.79	13.03	39.40	47.28
BAGHOUSE ASH	11.37	5.49	3.74	22.31	26.60	17.79	15.66	15.95	11.24	9.16
FLUE GAS	52.53	60.70	53.38	37.86	46.76	54.67	60.16	32.91	55.82	44.10
TOTAL OUTPUTS	78.12	84.51	69.09	109.27	105.49	106.41	94.61	61.90	106.47	100.54
BALANCE CLOSURE,%	103.81	101.12	107.26	107.50	95.30	103.73	97.00	90.36	99.20	101.04

TABLE A-11. MINERAL CARBON BALANCES

RUN NO.	2	4	6	7	8	10	11	11A	11B	11C
INPUTS,LB/HR MIN. C										
RETORTED SOLIDS	20.29	37.21	49.48	15.07	21.34	27.12	24.24	27.61	28.87	29.35
STEAM	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
AIR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NAT'L GAS	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
OVERFIRE AIR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
RETORT GAS	1.19	1.11	0.75	1.14	0.82	0.80	1.08	1.20	1.25	1.14
PURGES	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
RAW SHALE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TOTAL INPUTS	21.48	38.32	50.22	16.20	22.17	27.92	25.33	28.81	30.11	30.48
OUTPUTS, LB/HR MIN. C										
HEAT CARRIER	18.00	24.00	35.12	7.24	7.24	9.41	8.78	11.62	10.19	6.69
BAGHOUSE ASH	9.76	15.10	12.71	7.55	3.25	10.01	2.67	10.29	12.65	10.36
FLUE GAS	0.00	0.00	2.40	1.41	11.69	8.50	13.88	6.90	7.27	13.42
TOTAL OUTPUTS	27.76	39.10	50.23	16.20	22.18	27.92	25.33	28.81	30.11	30.47
BALANCE CLOSURE,%	129.28	102.03	100.01	99.99	100.06	100.00	100.02	100.01	100.01	99.97

RUN NO.	11D	12	13	14	17A	17B	17C	18	19C	20
INPUTS,LB/HR MIN. C										
RETORTED SOLIDS	34.90	34.40	28.92	56.58	49.79	39.60	41.36	32.43	53.88	55.42
STEAM	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
AIR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NAT'L GAS	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
OVERFIRE AIR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
RETORT GAS	0.92	1.17	0.72	1.29	0.00	0.00	0.00	1.59	0.00	1.45
PURGES	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
RAW SHALE	0.00	0.00	0.00	0.00	5.79	5.79	5.79	0.00	4.12	0.00
TOTAL INPUTS	35.83	35.58	29.64	57.87	55.58	45.39	47.15	34.02	58.00	56.87
OUTPUTS, LB/HR MIN. C										
HEAT CARRIER	9.83	13.05	9.43	42.08	29.10	32.13	18.79	13.03	35.77	43.95
BAGHOUSE ASH	10.33	4.31	2.74	16.85	20.27	14.71	13.70	14.29	10.54	8.87
FLUE GAS	15.66	18.42	17.47	0.00	6.21	0.00	14.66	6.69	11.69	4.05
TOTAL OUTPUTS	35.82	35.78	29.64	58.93	55.58	46.84	47.15	34.01	58.00	56.87
BALANCE CLOSURE,%	99.99	100.55	100.00	101.84	100.00	103.21	100.00	100.00	100.00	100.01

TABLE A-12. ORGANIC CARBON BALANCES

RUN NO.	2	4	6	7	8	10	11	11A	11B	11C
INPUTS,LB/HR ORG. C										
RETORTED SOLIDS	13.53	16.42	12.37	15.33	14.06	17.48	16.07	24.10	22.34	20.75
STEAM	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
AIR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NAT'L GAS	7.39	5.15	7.45	10.06	9.93	11.17	8.32	9.68	9.68	10.18
OVERFIRE AIR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
RETORT GAS	7.19	6.56	4.05	10.99	7.25	5.99	10.07	6.10	6.79	6.18
PURGES	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
RAW SHALE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TOTAL INPUTS	28.10	28.14	23.87	36.38	31.23	34.63	34.45	39.88	38.81	37.11
OUTPUTS, LB/HR ORG. C										
HEAT CARRIER	0.00	0.00	0.00	4.83	0.00	0.00	0.00	0.00	4.28	6.27
BAGHOUSE ASH	0.57	0.00	0.00	0.07	0.00	0.59	0.00	4.26	2.18	1.99
FLUE GAS	41.54	40.30	33.91	45.84	38.04	38.08	49.55	36.12	41.45	37.69
TOTAL OUTPUTS	42.10	40.30	33.91	50.73	38.04	38.67	49.55	40.38	47.91	45.95
BALANCE CLOSURE,%	149.85	143.24	142.08	139.46	121.78	111.65	143.82	101.26	123.43	123.84

RUN NO.	11D	12	13	14	17A	17B	17C	18	19C	20
INPUTS,LB/HR ORG. C										
RETORTED SOLIDS	24.36	27.52	18.55	29.36	24.37	26.28	20.15	19.03	23.49	25.50
STEAM	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
AIR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NAT'L GAS	10.37	10.61	10.18	8.75	9.00	9.19	8.50	8.50	10.37	10.80
OVERFIRE AIR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
RETORT GAS	4.70	9.86	6.04	5.67	0.00	0.00	0.00	6.95	0.00	6.34
PURGES	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
RAW SHALE	0.00	0.00	0.00	0.00	21.74	21.74	21.74	0.00	15.46	0.00
TOTAL INPUTS	39.42	48.00	34.77	43.78	55.11	57.20	50.39	34.49	49.32	42.64
OUTPUTS, LB/HR ORG. C										
HEAT CARRIER	4.39	5.27	2.53	7.01	3.03	1.82	0.00	0.00	3.64	3.33
BAGHOUSE ASH	1.04	1.18	1.01	5.46	6.32	3.08	1.96	1.66	0.70	0.29
FLUE GAS	36.87	42.28	35.91	37.86	40.55	54.67	45.50	26.22	44.13	40.05
TOTAL OUTPUTS	42.30	48.73	39.45	50.34	49.91	59.57	47.46	27.88	48.47	43.67
BALANCE CLOSURE,%	107.28	101.54	113.45	114.98	90.56	104.15	94.19	80.86	98.27	102.41

TABLE A-13. SULFUR BALANCES

RUN NO.	2	4	6	7	8	10	11	11A	11B	11C
INPUTS,LB/HR SULFUR										
RETORTED SOLIDS	9.88	20.11	26.41	15.33	13.54	16.27	15.48	12.30	11.04	12.40
STEAM	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
AIR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NAT'L GAS	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
OVERFIRE AIR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
RETORT GAS	0.41	0.30	0.15	1.60	2.16	0.77	0.36	0.93	0.90	0.82
PURGES	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
RAW SHALE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TOTAL INPUTS	10.30	20.41	26.56	16.93	15.69	17.04	15.84	13.23	11.94	13.21
OUTPUTS, LB/HR SULFUR										
HEAT CARRIER	9.66	16.10	22.83	13.17	11.63	10.71	11.04	8.36	8.76	8.57
BAGHOUSE ASH	4.64	4.61	3.60	4.93	5.76	5.23	5.07	4.91	5.02	5.29
FLUE GAS	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TOTAL OUTPUTS	14.30	20.71	26.43	18.10	17.40	15.94	16.11	13.27	13.78	13.86
BALANCE CLOSURE,%	138.82	101.46	99.52	106.94	110.84	93.52	101.66	100.34	115.42	104.91

RUN NO.	11D	12	13	14	17A	17B	17C	18	19C	20
INPUTS,LB/HR SULFUR										
RETORTED SOLIDS	12.05	15.48	13.91	30.80	25.42	23.13	17.32	17.63	17.96	19.72
STEAM	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
AIR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NAT'L GAS	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
OVERFIRE AIR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
RETORT GAS	0.71	1.16	2.40	1.07	0.00	0.00	0.00	0.64	0.00	0.59
PURGES	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
RAW SHALE	0.00	0.00	0.00	0.00	1.00	1.00	1.00	0.00	0.71	0.00
TOTAL INPUTS	12.77	16.64	16.31	31.87	26.42	24.12	18.32	18.27	17.96	20.31
OUTPUTS, LB/HR SULFUR										
HEAT CARRIER	8.99	11.04	10.35	26.78	22.73	20.00	13.94	14.25	16.37	15.46
BAGHOUSE ASH	4.91	5.45	6.52	3.86	4.32	4.90	5.65	5.16	3.51	3.43
FLUE GAS	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TOTAL OUTPUTS	13.90	16.49	16.87	30.63	27.05	24.91	19.59	19.41	19.88	18.89
BALANCE CLOSURE,%	108.86	99.12	103.39	96.13	102.39	103.25	106.93	106.24	110.70	93.03

TABLE A-14. NITROGEN ACCOUNTABILITY IN SOLIDS AND FLUE GAS NO_x

Test Number	2	4	6	7	8	10	11	11A	11B	11C	11D	12	13	14	17A	17B	17C	18	19C	20
Fluid Bed Temp,°F	1367	1250	1179	1558	1441	1363	1494	1428	1366	1384	1354	1424	1447	1134	1299	1376	1403	1367	1227	1268
Number of Combustion Stages	1	1	1	1	1	2	2	1	2	2	2	2	2	1	1	1	1	1	2	2
Input, % of Nitrogen in Solids to Combustor																				
Retorted Solids	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	81.8	76.7	71.4	100.0	77.2	100.0
Raw Shale	--	--	--	--	--	--	--	--	--	--	--	--	--	--	18.2	23.3	28.6	--	22.8	--
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Output, % of Nitrogen in Solids and Flue Gas NO_x from Combustor																				
Heat Carrier	42.3	35.1	70.1	50.8	0	28.7	0	20.4	62.6	66.1	47.5	73.0	60.2	63.7	25.9	16.7	10.1	21.3	22.8	22.4
Baghouse Ash	51.0	36.3	29.9	31.5	19.2	30.4	20.0	46.3	24.5	25.5	22.7	24.4	17.8	23.5	24.1	18.9	21.5	39.0	20.9	12.9
NO_x in Flue Gas	19.2	7.8	7.2	7.7	10.3	6.1	6.9	3.5	3.7	4.2	6.5	7.0	7.3	0.6	1.3	1.9	2.7	9.9	2.2	4.0
Unaccounted For	--	20.8	--	10.0	70.5	34.8	73.1	29.8	9.2	4.2	23.3	--	14.7	12.2	48.7	62.5	65.7	29.8	54.1	60.7
Total	112.5	100.0	107.2	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	104.4	100.0	100.0	100.0	100.0	112.5	100.0	107.2	100.0

TABLE A-15. MERCURY BALANCES AROUND COMBUSTOR

Inputs	Test 7		Test 12		Test 19C	
Retorted Solids, kg/hr	1178.1		1300.4		1566.7	
Hg, mg/hr		ND		14.30		ND
Retort Gas, m^3/hr	10.0		9.8			
Hg, mg/hr		ND		1.04		
Metal Spike, mg/hr				23,166.0		
Raw Shale, kg/hr					43.1	
Hg, mg/hr						0.64
Total Hg In, mg/hr				23,181.34		0.64
Outputs						
Heat Carrier, kg/hr	995.6		1138.1		1374.8	
Hg, mg/hr		ND		76.32		ND
Baghouse Ash, kg/hr	154.2		136.1		157.8	
Hg, mg/hr		1.40		285.80		3.00
Flue Gas, m^3/hr	410		387			
Hg, mg/hr		ND		9566.40	398	8.76
Total Hg Out, mg/hr		1.40		9928.52		11.76
Recovery, %				42.8		1838

ND = Not detected.

TABLE A-16. CADMIUM BALANCES AROUND COMBUSTOR

Inputs	Test 7		Test 12		Test 19C	
Retorted Solids, kg/hr	1178.1		1300.4		1566.7	
Cd, mg/hr		1.025		29.909		2.193
Retort Gas, m^3/hr	10.0		9.8			
Cd, mg/hr		0.002		0.003		
Metal Spike, mg/hr				23.166		
Raw Shale, kg/hr					43.1	
Cd, mg/hr						0.030
Total Cd In, mg/hr		1.027		23,181.34		2.223
Outputs						
Heat Carrier, kg/hr	995.6		1138.1		1374.8	
Cd, mg/hr		0.856		76.32		2.200
Baghouse Ash, kg/hr	154.2		136.1		157.8	
Cd, mg/hr		0.108		285.80		1.436
Flue Gas, m^3/hr	410		387			
Cd, mg/hr		0.011		9566.40	398	0.006
Total Cd Out, mg/hr		0.975		34.2652		3.642
Recovery, %		95		64.6		164

TABLE A-17. ARSENIC BALANCES AROUND COMBUSTOR

Inputs	Test 7		Test 12		Test 19C	
Retorted Solids,kg/hr	1178.1		1300.4		1566.7	
As, g/hr		42.41		48.11		65.80
Retort Gas, m^3/hr	10.0		9.8			
As, g/hr		1.15		0.86		
Raw Shale, kg/hr					43.1	
As, g/hr						2.33
Total As In, g/hr		43.56		48.97		68.13
Outputs						
Heat Carrier, kg/hr	995.6		1138.1		1374.8	
As, g/hr		46.79		35.28		48.12
Baghouse Ash, kg/hr	154.2		136.1		157.8	
As, g/hr		13.88		12.52		11.36
Flue Gas, m^3/hr	410		387		398	
As, g/hr		0.003		0.003		0.004
Total As Out, g/hr		60.673		47.803		59.484
Recovery, %		139		97.6		87.3

TABLE A-18. LEAD BALANCES AROUND COMBUSTOR

Inputs	Test 7		Test 12		Test 19C	
Retorted Solids,kg/hr	1178.1		1300.4		1566.7	
Pb, g/hr		28.27		31.21		42.30
Retort Gas, m^3/hr	10.0		9.8			
Pb, g/hr		0.03		0.001		
Raw Shale, kg/hr					43.1	
Pb, g/hr						1.29
Total Pb In, g/hr		28.30		31.211		43.60
Outputs						
Heat Carrier, kg/hr	995.6		1138.1		1374.8	
Pb, g/hr		21.90		25.03		35.74
Baghouse Ash, kg/hr	154.2		136.1		157.8	
Pb, g/hr		3.08		3.27		3.95
Flue Gas, m^3/hr	410		387		398	
Pb, g/hr		0.05		0.002		0.05
Total Pb Out, g/hr		25.03		28.302		39.74
Recovery, %		88.4		90.7		91.2

TABLE A-18. LEAD BALANCES AROUND COMBUSTOR

Inputs	Test 7		Test 12		Test 19C	
Retorted Solids, kg/hr	1178.1		1300.4		1566.7	
Pb, g/hr		28.27		31.21		42.30
Retort Gas, m^3/hr	10.0		9.8			
Pb, g/hr		0.03		0.001		
Raw Shale, kg/hr					43.1	
Pb, g/hr						1.29
Total Pb In, g/hr		28.30		31.211		43.60
Outputs						
Heat Carrier, kg/hr	995.6		1138.1		1374.8	
Pb, g/hr		21.90		25.03		35.74
Baghouse Ash, kg/hr	154.2		136.1		157.8	
Pb, g/hr		3.08		3.27		3.95
Flue Gas, m^3/hr	410		387		398	
Pb, g/hr		0.05		0.002		0.05
Total Pb Out, g/hr		25.03		28.302		39.74
Recovery, %		88.4		90.7		91.2

TABLE A-19. BERYLLIUM BALANCES AROUND COMBUSTOR

Inputs	Test 7		Test 12		Test 19C	
Retorted Solids, kg/hr	1178.1		1300.4		1566.7	
Be, g/hr		0.566		0.832		1.003
Retort Gas, m^3/hr	10.0		9.8			
Be, g/hr		ND		ND		
Raw Shale, kg/hr					43.1	
Be, g/hr						0.029
Total Be In, g/hr		0.566		0.832		1.032
Outputs						
Heat Carrier, kg/hr	995.6		1138.1		1374.8	
Be, g/hr		0.677		0.592		0.770
Baghouse Ash, kg/hr	154.2		136.1		157.8	
Be, g/hr		0.157		0.147		0.196
Flue Gas, m^3/hr	410		387		398	
Be, g/hr		0.004		ND		ND
Total Be Out, g/hr		0.838		0.739		0.966
Recovery, %		148		88.7		93.6

ND = Not detected.

TABLE A-20. FLUORIDE BALANCES AROUND COMBUSTOR

Inputs	Test 7		Test 12		Test 19C	
Retorted Solids, kg/hr	1178.1		1300.4		1566.7	
F, g/hr		282.7		429.1		642.3
Retort Gas, m^3/hr	10.0		9.8			
F, g/hr		ND		ND		
Raw Shale, kg/hr					43.1	
F, g/hr						31.5
Total F In, g/hr		282.7		429.1		673.8
Outputs						
Heat Carrier, kg/hr	995.6		1138.1		1374.8	
F, g/hr		230.0		330.0		481.2
Baghouse Ash, kg/hr	154.2		136.1		157.8	
F, g/hr		107.9		121.1		123.1
Flue Gas, m^3/hr	410		387		398	
F, g/hr		ND		ND		ND
Total F Out, g/hr		337.9		451.1		604.3
Recovery, %		119		105		89.7

ND = Not detected.

APPENDIX B

LEACHING AND HYDRAULIC PROPERTIES OF THREE BAGHOUSE ASH SAMPLES

APPENDIX B

LEACHING AND HYDRAULIC PROPERTIES OF THREE BAGHOUSE ASH SAMPLES

by

Dr. David B. McWhorter
Colorado State University

A. INTRODUCTION

Three samples of baghouse ash were provided to Colorado State University for the measurement of the leaching and hydraulic properties. The samples tested were designated by run number and sample number and are, respectively: 11-54591, 14-54592, and 17B-54593. The operating conditions of the retort, fluid bed combuster, and retort gas under which these materials were produced are presented elsewhere in this report.

One purpose of the tests made at Colorado State University was to provide information on the potential changes in the leaching characteristics of retorted oil shale that has undergone the fluid bed combustion and other treatments as described previously in this report. This is accomplished by comparing the results from ESM tests (McWhorter and Durnford, 1986) on the ash samples with results from a similar test on material produced by the TOSCO-II retorting process. While the results are not rigorously comparable because the final products did not derive from identical feed stock, etc., the comparison remains useful as an indication of any significant changes that may occur.

The hydraulic properties of the ash samples were measured to determine if these materials exhibited any extraordinary characteristics not observed previously in similar measurements on combusted shales. Hydraulic properties of porous media are highly variable and sensitive to many parameters unrelated to the combustion and sulfur adsorption treatments to which these particular materials were subjected. It is, therefore, not possible to attribute quantitative differences between the properties of the ash samples and the corresponding properties of TOSCO-II retorted shales solely to the fluid bed combustion and sulfur adsorption treatments received by the ash samples.

B. LEACHING EXPERIMENTS

The Equilibrated Soluble Mass (ESM)(Nazareth, 1984; McWhorter and Durnford, 1986) test was used in this project as a method for characterizing the leaching properties of the baghouse ash samples. This equilibrated pore solution is subsequently displaced by injection of distilled water. The salient feature of this test is that the chemical composition of the first effluent from the column is that which evolved during the equilibration period under conditions of liquid-to-solid ratio and aeration the are similar to those expected under field conditions.

In the ESM column leaching test, the sample is moistened with distilled water. The moisturizing process is performed by weighing out a dry sample to a given dry bulk density and sprinkling the sample with a weighed quantity of deionized water. During the sprinkling process, the sample is continually mixed to distribute the water evenly, and both the water added and the total weight of the solid-liquid mixture is monitored. After the moisturizing process is complete, the moisturized sample equilibrates for 72 hours in a closed environment before the column is packed and the leaching test run.

The columns used in this study were 42-43 cm long with diameters of about 10 cm. The columns were packed in lifts to minimize separation and layering. Although each of the ash samples was packed as densely as possible, achieving densities much higher than 1.0 g/cc proved difficult. The #11 Baghouse Ash, particularly, was very difficult to pack because it had very little cohesiveness.

The leaching test is performed by injecting distilled water at a constant rate into the bottom of the column. Bottom injection minimizes air entrapment and piping. The bottom and top end-plates of the column have 2 mm conical disks machined onto the surfaces that promote uniform flow over the cross section of the column and insure mixing of the effluent as it enters and exits the column. Perforated rigid disks support the material and filter disks on the top and bottom prevent movement of the fines through the end plates. A rubber ring seals the top plate to the column body.Effluent from the top of the column is routed through an electrical conductivity probe and pH meter and into a graduated cylinder. A record of the cumulative volume of outflow, time, pH, EC, and inflow pressure is maintained. Effluent samples are collected and saved at intervals for chemical analyses.

Table B-1 summarizes the significant parameters for the ESM test for the three baghouse samples tested in this study. Two values for initial moisture contents are given in the table. The reason for this is that the samples hydrated during the equilibration period, particularly #11 and #17. The #11 Baghouse Ash sample was weighed and moisturized at 17 percent distilled water by weight. After the moisturizing procedure was completed and the sample container sealed, the temperature of the sample rose to 43°C after ten minutes and to maximum of 48°C in twenty minutes. The ambient temperature was 22°C. During column packing 72 hours later, moisture contents of the

TABLE B-1. ESM COLUMN LEACH TEST PARAMETERS

Sample	Baghouse Ash #11	Baghouse Ash #14	Baghouse Ash #17
1. Packed Volume (cm^3)	3282	3267	3390
2. Initial Moisture Content, % by weight added to dry sample*	17.0	17.0	17.0
3. Initial Moisture Content, % by weight determined by oven drying after equilibration period*	10.6	15.5	13.3
4. Dry Bulk Density (kg/m^3)**	1025	1185	1010
5. Effective Particle Density (kg/m^3)	3052	2754	2908
6. Porosity	0.664	0.570	0.653
7 Flowrate (ml/hr)	120.0	144.8	161.8
8. Total Time after outflow (hrs)	22.7	23.2	24.1

*Difference between moisture added and moisture found by oven drying is due to hydration during 72 hour equilibration period.

**Dry Bulk Density is based on moisture content by oven drying given in 3.

equilibrated sample were determined by standard oven drying methods and found to be 10.6, and 10.7, and 10.4 percent by weight, indicating that significant hydration had occurred. Similar data were collected for the #17 sample tested. A temperature change from 22°C to 42°C was noted for the #17 Baghouse Ash with a consequent drop in moisture content during the equilibrium period from 17 percent to 13.3 percent by weight. The #14 Baghouse Ash had a measured moisture content change from 17 to 15.5 percent (the average of three samples) but no change in temperature was noted. Dry bulk densities shown in Table B-1 are based on final moisture contents.

C. RESULTS OF LEACHING TESTS

Tables B-2, B-3, and B-4 contain the data for the chemical composition of the column effluent for the three samples. Figures B-1, B-2 and B-3 show the variation of the electrical conductivity as a function of effluent volume.

As has been the case for practically all of the retorted and combusted shales subjected to the ESM test, the initial column effluent is quite saline. Furthermore, the overall levels of individual dissolved constituents are not remarkably different from those that have been observed in effluent from other combusted shale materials. A second index to the leachability is the volume of effluent required to achieve a 50 percent relative electrical conductivity in the effluent. Theoretical considerations (Nazareth, 1984) show that if all of the leachable solids are dissolved in the initial moisturizing waters, then the 50 percent relative electrical conductivity should occur at an effluent volume equal to the volume of moisture used in the initial equilibration. Occurrence of the 50 percent relative electrical conductivity at a volume greater than this value indicates the presence of significant solubility controls and the tendency for leaching to occur more slowly. All of the baghouse ashes resulted in 50 percent relative concentrations at effluent volumes near the volume of initial moisturizing waters.

The plots of relative electrical conductivity (Figures B-1, B-2, and B-3) show a tendency toward a constant relative EC of about 20 percent as the effluent volume becomes larger. Again, this is a characteristic observed in many other such tests.

Table B-5 provides data for a direct comparison of the concentrations of selected species in effluent from the ash samples and from TOSCO-II retorted shale. The first portion of the table compares data from samples of the initial effluent; the second portion compares data from samples at about the same effluent volumes collected after leaching was well advanced. Perhaps the only remarkable differences in the results are the much higher concentrations of potassium in the first effluents from the combusted shales and the much lower magnesium concentration. The concentration of other constituents, while certainly not the same, are not so different that the ash samples would be put in another category with respect to leaching. Significantly, the sulfate concentrations derived from the ash samples are not greater than from

TABLE B-2. ESM TEST RESULTS FOR SAMPLE 11-54591

Parameter	Effluent Volume/Pore Volume				
	0.03	0.09	0.25	0.41	0.62
pH	13.0	12.8	12.1	11.8	11.7
EC,ds/m	53.2	42.6	15.1	11.3	10.6
TDS,mg/l	35720	26980	6850	5050	5140
Ca,mg/l	647	679	1020	1290	1300
Mg,mg/l	<1	<1	<1	<1	<1
Na,mg/l	8850	6360	817	162	146
K,mg/l	4820	2990	272	96	90
SO_4,mg/l	18380	13120	2140	1220	1130
Cl,mg/l	83	71	25	17	17
NO_3,mg/l	11	9	4	3	3
NH_4,mg/l	92	22	6	6	6
CO_3,mg/l	1080	1040	722	395	925
OH,mg/l	1810	1480	620	633	300
F,mg/l	5.4	4.7	2.4	2.0	1.7
Al,mg/l	0.10	0.22	0.16	0.30	0.25
Fe,mg/l	0.02	0.02	0.02	0.12	0.07
Mn,mg/l	0.01	0.02	0.02	0.02	0.02
Cu,mg/l	0.18	0.02	0.04	0.08	0.06
Zn,mg/l	0.15	0.02	0.01	0.03	0.03
Ni,mg/l	<0.01	<0.01	<0.01	<0.01	<0.01
Mo,mg/l	4.29	2.47	0.62	0.27	0.29
Cd,mg/l	<0.01	<0.01	<0.01	<0.01	<0.01
Cr,mg/l	2.99	1.66	0.46	0.28	0.27
Sr,mg/l	38.1	38.3	38.3	38.3	38.3
B,mg/l	0.55	1.60	1.07	1.84	1.74
Ba,mg/l	0.21	0.20	0.24	0.31	0.34
Pb,mg/l	<0.05	<0.05	<0.05	<0.05	<0.05
Hg,mg/l	<0.001	<0.001	<0.001	<0.001	<0.001
As,mg/l	0.006	<0.001	0.003	0.003	0.001
Se,mg/l	0.210	0.118	0.025	0.012	0.011

TABLE B-3. ESM TEST RESULTS FOR SAMPLE 14-54591

Parameter	Effluent Volume/Pore Volume					
	0.04	0.11	0.28	0.44	0.60	0.90
pH	12.5	12.6	12.5	12.2	12.1	11.9
EC,ds/m	25.7	25.7	18.9	9.5	6.4	5.4
TDS,mg/l	20570	20330	13810	6680	4660	4310
Ca,mg/l	597	571	397	689	792	774
Mg/mg/l	<1	<1	<1	<1	<1	<1
Na,mg/l	5420	5320	3380	992	298	196
K,mg/l	691	635	469	236	132	89
SO_4,mg/l	10640	10620	6930	2740	1670	1560
Cl,mg/l	414	336	273	142	85	96
NO_3,mg/l	11	11	9	6	5	4
NH_4,mg/l	113	109	58	39	33	33
CO_3,mg/l	1350	1510	835	519	288	220
OH,mg/l	198	83	278	121	163	141
F,mg/l	13.4	13.8	11.7	8.8	6.9	6.2
Al,mg/l	0.56	0.59	0.46	0.37	0.39	0.29
Fe,mg/l	0.02	0.03	0.02	0.09	0.28	0.06
Mn,mg/l	0.01	0.02	0.02	0.02	0.02	0.02
Cu,mg/l	0.21	0.14	0.06	0.04	0.03	0.02
Zn,mg/l	0.03	0.04	0.01	0.02	0.03	0.02
Ni,mg/l	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Mo,mg/l	23.70	23.60	14.90	6.10	3.60	3.30
Cd,mg/l	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cr,mg/l	0.13	0.13	0.08	0.07	0.07	0.05
Sr,mg/l	19.3	19.6	20.3	22.6	24.5	25.2
B,mg/l	1.16	1.44	1.86	1.89	1.93	1.77
Ba,mg/l	0.13	0.13	0.13	0.14	0.15	0.16
Pb,mg/l	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Hg,mg/l	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
As,mg/l	0.039	<0.044	<.008	0.012	0.010	0.008
Se,mg/l	0.242	0.256	0.140	0.053	0.034	0.032

TABLE B-4. ESM TEST RESULTS FOR SAMPLE 17-54591

Parameter	Effluent Volume/Pore Volume				
	0.03	0.07	0.19	0.33	0.66
pH	13.3	13.2	13.0	12.6	12.4
EC,ds/m	53.3	52.3	34.1	14.1	10.2
TDS,mg/l	17010	16120	9742	4370	3540
Ca,mg/l	150	167	154	557	723
Mg/mg/l	<1	<1	<1	<1	<1
Na,mg/l	5810	5470	3070	689	186
K,mg/l	1870	1730	1040	284	113
SO_4,mg/l	2840	2460	1030	203	59
Cl,mg/l	231	171	89	20	11
NO_3,mg/l	2	1	1	<1	1
NH_4,mg/l	132	93	31	22	24
CO_3,mg/l	1440	1310	970	677	790
OH,mg/l	3430	3570	2150	697	409
F,mg/l	18.8	15.4	7.7	3.8	2.8
Al,mg/l	0.32	0.26	0.17	0.24	0.17
Fe,mg/l	0.02	0.01	0.01	0.01	0.01
Mn,mg/l	<0.01	0.01	0.01	0.01	0.01
Cu,mg/l	0.29	0.12	0.02	0.01	0.01
Zn,mg/l	0.33	0.13	0.02	0.01	0.02
Ni,mg/l	<0.01	<0.01	<0.01	<0.01	<0.01
Mo,mg/l	5.30	4.20	1.80	0.37	0.14
Cd,mg/l	<0.01	<0.01	<0.01	<0.01	<0.01
Cr,mg/l	0.05	0.05	0.05	0.05	0.05
Sr,mg/l	12.0	14.9	26.0	37.3	37.3
B,mg/l	1.02	0.56	1.70	1.49	1.63
Ba,mg/l	0.25	0.33	0.52	1.31	2.34
Pb,mg/l	<0.05	<0.05	<0.05	<0.05	<0.05
Hg,mg/l	<0.001	<0.001	<0.001	<0.001	<0.001
As,mg/l	0.022	0.014	0.001	<0.001	0.001
Se,mg/l	0.043	0.032	0.016	0.005	0.015

TABLE B-5. COMPARISON OF EFFLUENTS FROM ASH SAMPLES AND TOSCO-II RETORTED SHALE

Initial Effluent

Parameter	11-54591	14-54592	17-B-54593	TOSCO-II
EC,ds/m	53.2	25.7	53.2	36.5
pH	13.0	12.5	13.3	9.3
Na,mg/l	8850	5420	5810	9910
Ca,mg/l	647	597	150	368
Mg,mg/l	<1	<1	<1	695
K,mg/l	4820	691	1870	109
SO_4,mg/l	18380	10640	2840	28510
Cl,mg/l	83	414	231	218
F,mg/l	5.4	13.4	18.8	24.9
MO,mg/l	4.3	23.7	5.3	26.3

Final Effluent

Parameter	11-54591	14-54592	17-B-54593	TOSCO-II
EC,ds/m	10.6	5.4	10.2	6.6
pH	11.7	11.9	12.4	-
Na,mg/l	146	196	186	1160
Ca,mg/l	1300	774	723	62
Mg,mg/l	<1	<1	<1	83
K,mg/l	90	89	113	15.4
SO_4,mg/l	1130	1560	59	3132
Cl,mg/l	17	96	11	8.9
F,mg/l	1.7	6.2	2.8	22.0
MO,mg/l	0.29	3.3	0.14	5.4

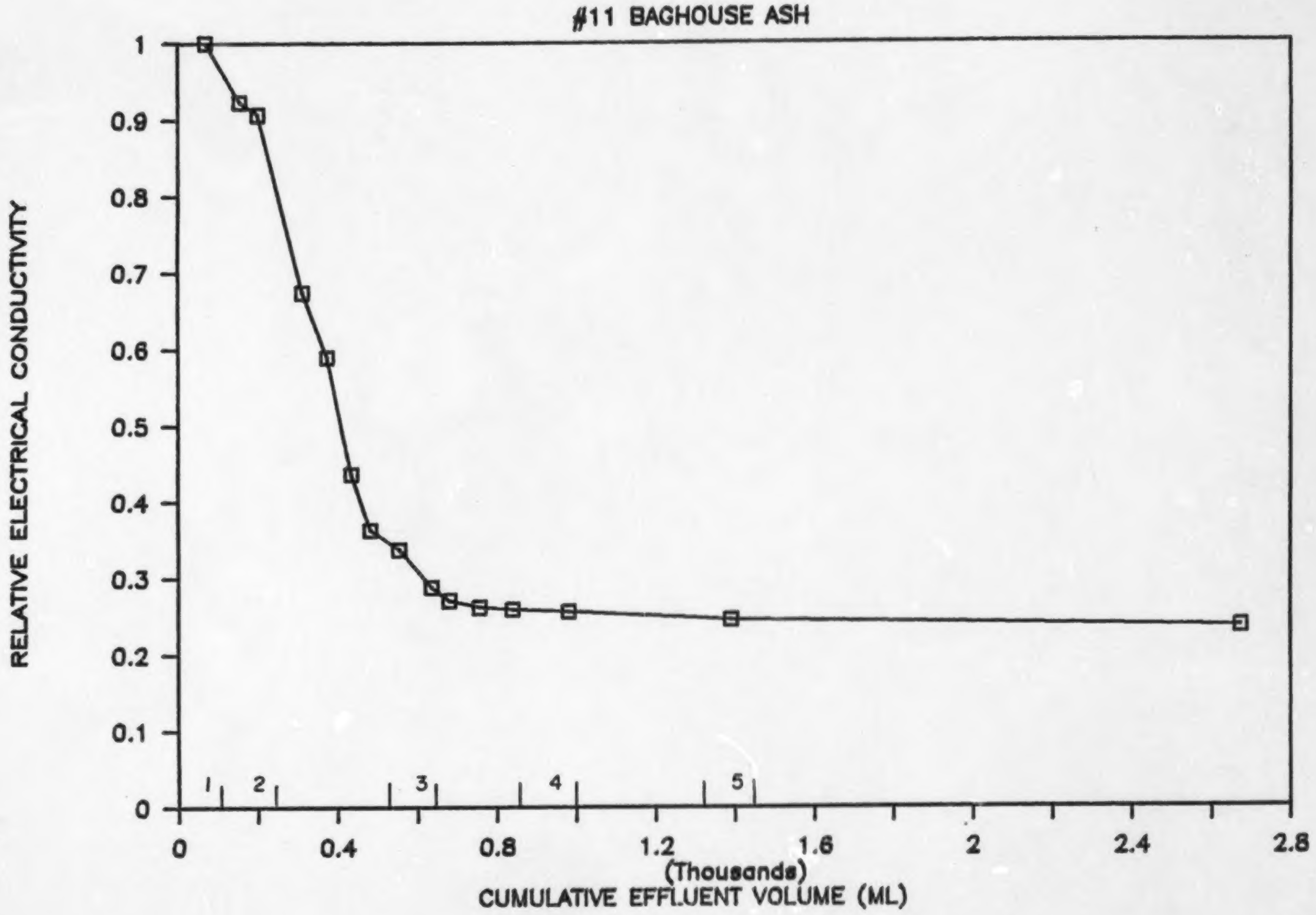

Figure B-1. Relative electrical conductivity curve, #11.

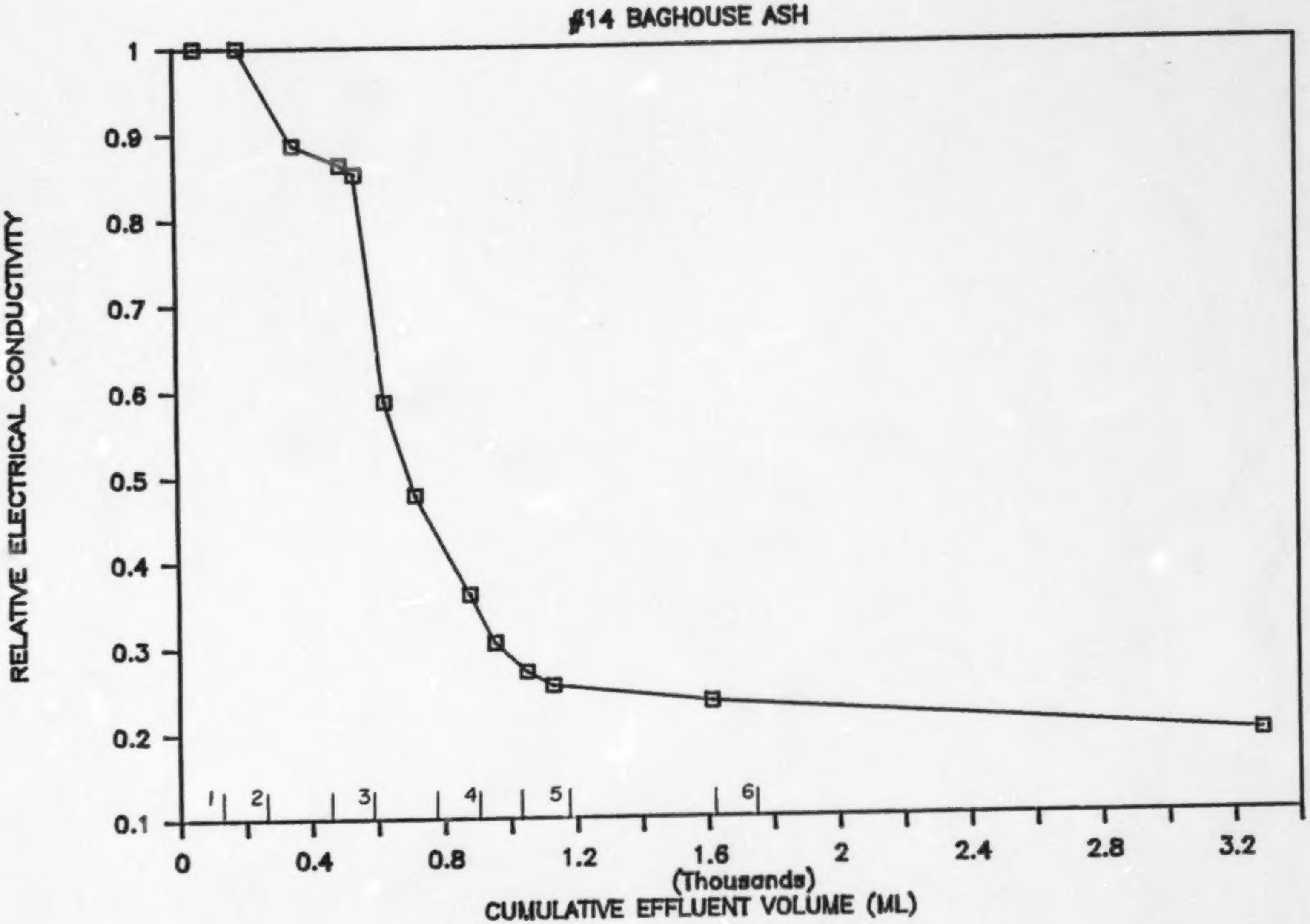

Figure B-2. Relative electrical conductivity curve, #14.

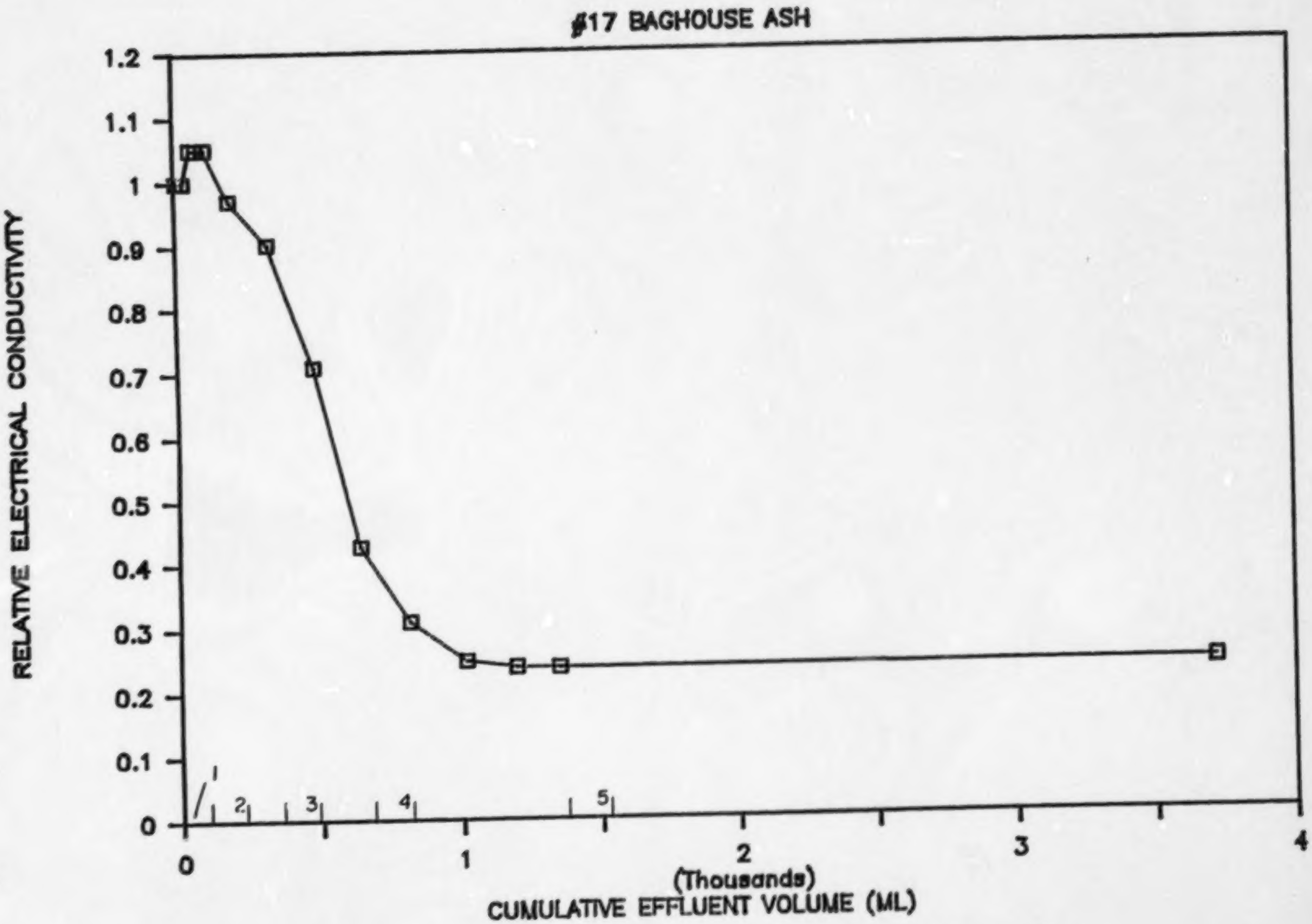

Figure B-3. Relative electrical conductivity curve, #17.

the TOSCO-II retorted material. Overall, the data suggest that adsorption of chemicals (primarily sulfur) from the flue gas did not substantially modify the levels or amounts of most constituents that are leached from the shale by this test.

D. HYDRAULIC PROPERTIES

Particle Density-The particle densities of all three materials were measured at 500 ml volumetric flasks. Duplicate samples of the material were wetted under vacuum to insure removal of entrapped air. Due to the high mass of soluble salts in the samples, the calculations of the particle density were corrected for the sample mass in solution. This was done by measuring the total dissolved solids (T.D.S.) in the flask solution, calculating the total dissolved mass and then reducing initial sample mass by that amount. Without that correction unreasonably high values of particle density would have been obtained.

Water Characteristics-The water characteristic of a material is a measure of the material's ability to hold capillary and adsorbed water at pressures less than atmospheric and water contents less than saturation. The amount of water held at a given capillary pressure is a function of whether the material is drying or wetting. Only the wetting characteristics were measured. The method used was consistent with ASTM D2352 except water was circulated beneath the plate to provide a source to wet the samples. Figure B-4 presents the results of the analysis.

Hydraulic Diffusivity-Using the theory of hydraulic diffusivity the unsaturated hydraulic conductivity of a porous medium can be measured. The hydraulic diffusivity is defined as:

$$D(\theta) = K(\theta) dh/d\theta \qquad (1)$$

where $D(\theta)$ = hydraulic diffusivity (L^2/T)

$K(\theta)$ = hydraulic conductivity (L/T)

θ = volumetric water content

h = capillary pressure (L)

The relation $dh/d\theta$ is the slope of the water holding capacity curve. With this relationship, Darcy's law for one-dimensional horizontal flow can be stated as

$$q = - D(\theta) \partial\theta/\partial x \qquad (2)$$

Bruce and Klute (1956) showed that $D(\theta)$ can be measured in an unsteady flow cell. A horizontal column is wetted from a constant pressure source for a relatively short period and then the water content along the column is determined. The diffusivity is calculated by:

$$D(\theta_x) = - \frac{1}{2} \frac{d\lambda}{d\theta} \bigg|_{\theta_x} \int_{\theta_i}^{\theta} \lambda \, d\theta \qquad (3)$$

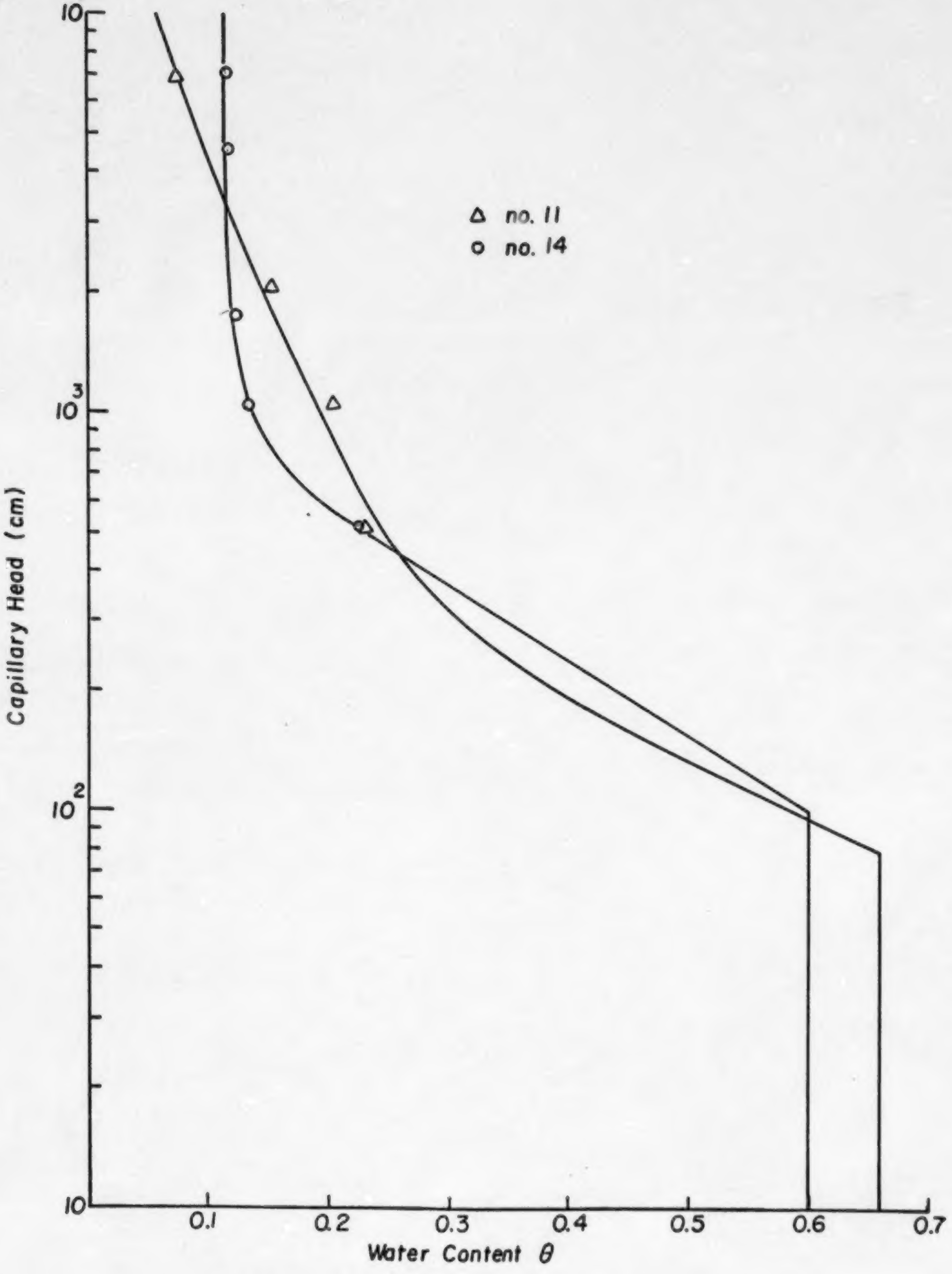

Figure B-4. Water characteristics.

where θ_i = initial water content

$\lambda = x/t^{1/2}$

This method has the advantage that data collected at different times is normalized to yield a single curve.

For materials #11 and #14, columns at initial water contents of about 10 percent by weight were run. Water contents at various times were measured by gamma attenuation. The diffusivities for each density were then calculated using Eq. (3). Figure B-5 presents the diffusivities for each material. The values are reasonable for the material and densities.

Hydraulic Conductivity-The unsaturated hydraulic conductivity can be determined using the relation:

$$K(\theta) = D(\theta)\, d\theta/dh \qquad (4)$$

The term $d\theta/dh$ is the inverse of the slope of the water characteristic. Using this relationship and the measured water characteristics and diffusivities, the unsaturated conductivities were computed. Figure B-6 presents the results. The ranges are reasonable for the materials and densities.

Saturated Hydraulic Conductivity-The saturated hydraulic conductivity of samples #11 and #14 were determined with a falling head permeameter. Columns approximately 3.7 cm in diameter, 15 cm long with a flexible membrane between the sample and column wall were used. During testing, the region between the membrane and column wall was slightly pressurized to ensure no seepage along the walls. Maximum hydraulic gradients used were 6 for sample #14 and 16 for sample #11.

Sample #14 was tested for three days. During that period, the hydraulic conductivity was constant at 1.7×10^{-5} cm/s. Sample #11, due to its cementing characteristics, was tested twice. The first column was packed immediately after moisturizing. It had a conductivity which declined over the next 10 days from $4 \times {}^{-7}$ cm/s to 2×10^{-8} cm/s. The second column was packed after three days of curing. It had a constant conductivity of 2.6×10^{-5} cm/s.

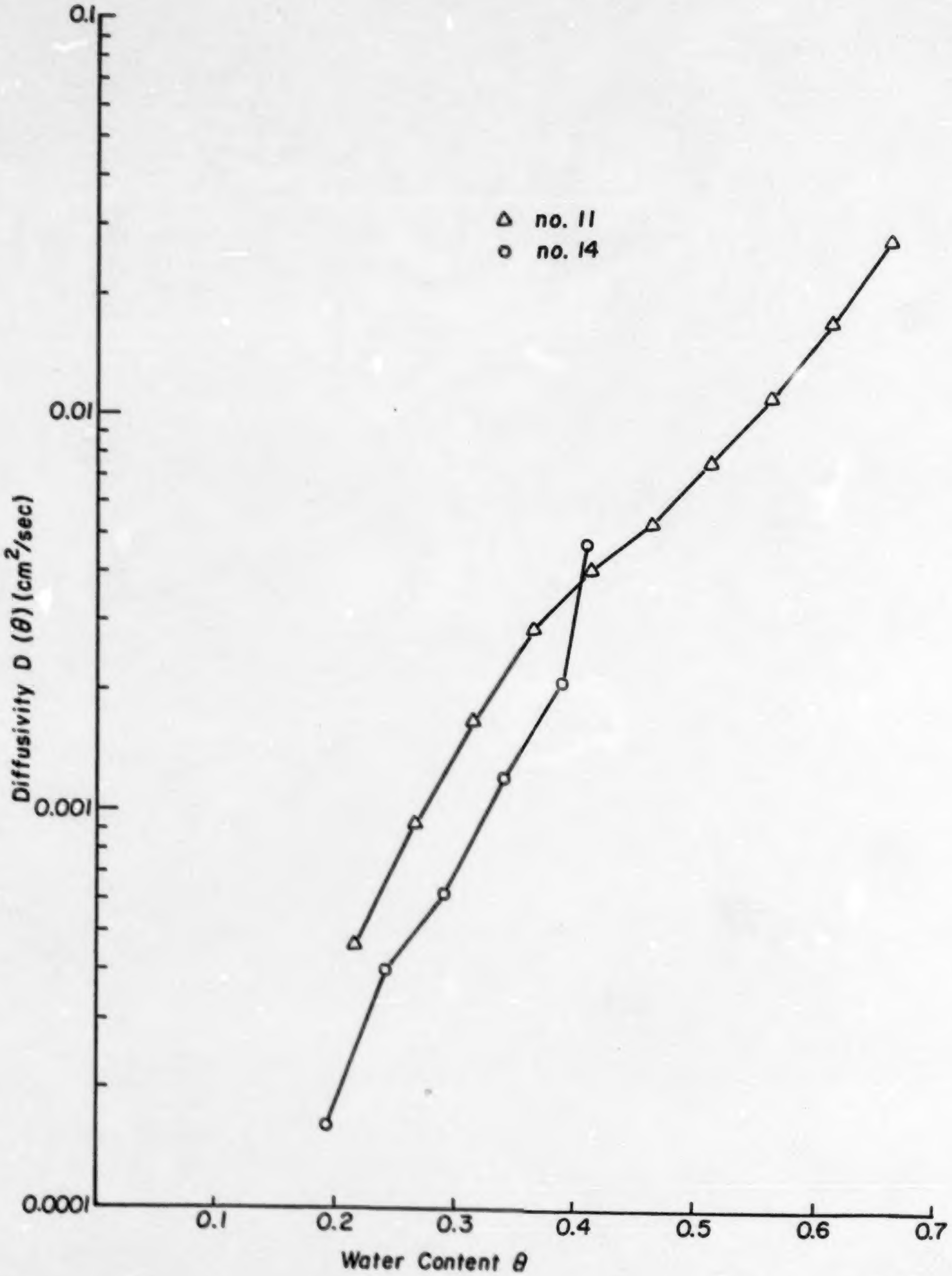

Figure B-5. Hydraulic diffusivities.

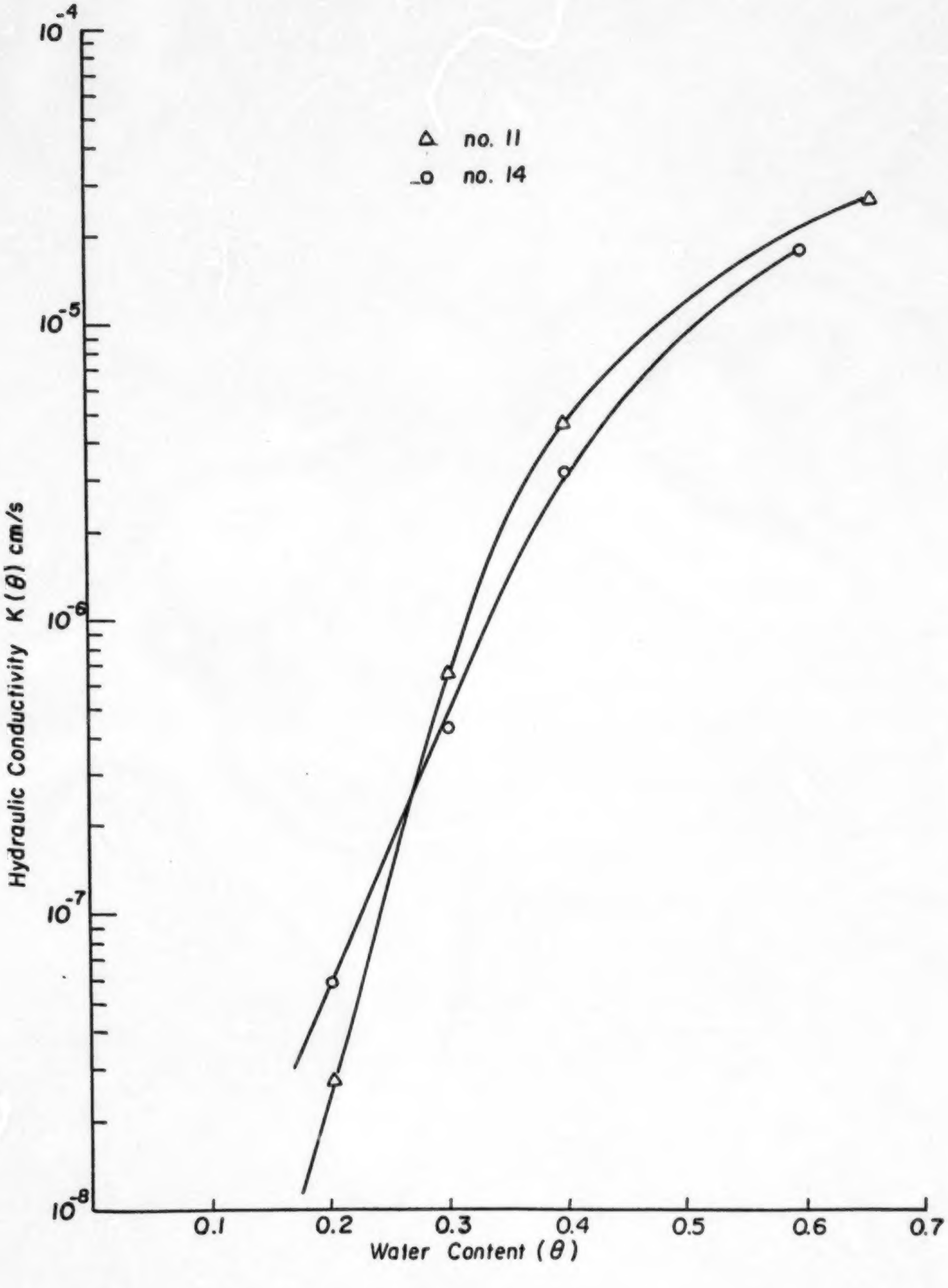

Figure B-6. Hydraulic conductivity.

REFERENCES

1. Bruce, R.R. and A. Klute. 1956. The measurement of soil-moisture diffusivity. Soil Sci. Soc. Am. Proc., Vol. 20, pp. 458-462.

2. McWhorter, D.B. and Durnford, D.S. Leaching and hydraulic properties of retorted oil shale including effects from codisposal of wastewater. Final Report on Cooperative Agreement CR-807668, USEPA/AEERL-202, 180 p.

3. Nazareth, V.A. 1984. A Laboratory Column Leach Test for Oil Shale Solid Wastes. Ph.D. Dissertation, Colorado State University, Fort Collins, CO.